SURFACE RADIOCHEMISTRY.

THESIS

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by

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ABSTRACT

The retention of hydrocarbons by alumina-supported catalysts of palladium, rhodium and platinum has been investigated in the temperature range 20 to 200°C using a microcatalytic-radiochromatographic technique.

The retention, by a 5% Pd/Al_2O_3 catalyst, of methane, ethane, propane, ethylene, propylene, acetylene and cyclopropane indicates that the carbon-carbon bond type is the most important feature in determining the amount of retention which takes place. The following order was established.

$$C_2H_2 > C_2H_4 \approx C_3H_6 > C_3H_8 \approx C_2H_6 \approx CH_4$$

An investigation of the source of the hydrogen in the alkanes recovered from the injection of unsaturated hydrocarbons in these experiments was conducted using tritium in the reduction of the palladium, rhodium and platinum catalysts. Subsequent injections of ethylene and acetylene indicate that both self-hydrogenation and hydrogen remaining after catalyst reduction are responsible for the alkane production: this hydrogen cannot be removed from the catalyst in a flow of helium at 200°C. The dependence on self-hydrogenation is at a minimum for palladium, and it is considered that this is attributable to the ability

of this metal to accommodate hydrogen interstitially.

The variation of ethylene retention with catalyst shows the following trend at 100° and 200°C.

$$Rh > Pt > Pd$$

Correlation of this order with other catalytic properties and the evidence of self-hydrogenation suggest that the retention is due to dissociatively adsorbed residues e.g.

$$\begin{array}{l} HC = CH \\ \;\;|\quad\;\; | \\ \;\;*\quad\;\; * \end{array}$$

A further investigation of the retained species from adsorption using C-14 ethylene shows that it is inactive in hydrogenation and molecular exchange and cannot be displaced from the catalysts by acetylene although the acetylene is adsorbed. A simple associatively bonded acetylene structure similar to the one above is therefore considered unlikely and the existence of polymeric surface structures seems more probable.

The extent of the retention of ethylene and acetylene observed on all three catalysts is in excess of monolayer coverage as calculated from the metal areas determined by carbon monoxide adsorption. This result is considered in terms of metal surface heterogeneity and adsorption on the alumina support material.

CONTENTS

CHAPTER ONE

AN INTRODUCTION

1.1 Introduction.

Two main mechanisms have been postulated for the reaction between two gases at a solid surface. In the Langmuir-Hinshelwood[1] mechanism both reactants are considered to be chemisorbed on the surface; in the Rideal-Eley[2] mechanism one reactant is considered to be chemisorbed and the other physically adsorbed. It can therefore be appreciated that an understanding of chemisorption is necessary before catalytic activity and the bulk properties of catalytic materials might be correlated.

Of the two adsorption types, physical adsorption and chemisorption, the latter always involves stronger adsorbent-adsorbate bonds (10-100kcal.mole^{-1}) and may involve a small activation energy. The absence of this is not alone a sufficient criterion for physical adsorption. Catalytic solids have been shown, in many experiments and by a variety of techniques, to be heterogeneous with respect to chemisorption. The observed nature and possible sources of this heterogeneity are the subjects of much published work and an attempt is made in this chapter to summarise and evaluate the observations made, with particular emphasis on hydro-

-carbon adsorption on transition metals.

1.2 Evidence for Surface Heterogeneity.

Taylor postulated his "active site theory" in 1925[3] and although the earliest experimental evidence was a demonstration that poisoning affected reaction to a much greater extent than adsorption,[4] most of the work between 1925 and 1945 was on rates of adsorption at different temperatures and of a general calorimetric nature. Different authors attributed the principal finding, a decrease in the heat of adsorption with increasing surface coverage, to -

(a) an inherent heterogeneity of the surface e.g. crystallite edges or defects.[5]

(b) interaction between the reactant and those species already adsorbed i.e. the dipole-dipole effect.[6]

(c) an induced surface heterogeneity caused by the initially adsorbed material increasing the work function of the remaining surface.[7]

Bond,[8] summarising the evidence from this type of experiment in 1962, concluded that heterogeneities of types (a) and (c) would be found together and would be more important than type (b).

Isotopes have been used in the study of adsorption

in at least two distinct ways, the differential technique and the kinetic technique. The latter method embraces the profusion of work published on exchange reactions, evidence from which will be considered below. The former method first employed by Keier and Roginskii provides much more direct evidence of heterogeneity than the calorimetric studies described above. The adsorption is carried out in two or more steps using gases of different isotopic abundances. Investigation of the isotope content of gases removed in successive stages of desorption demonstrates heterogeneity if the fraction of gas desorbed first has a similar isotopic abundance to that adsorbed last. Using this technique, Keier and Roginskii[9] observed the heterogeneity of charcoal, nickel[10] and zinc oxide[10] to hydrogen chemisorption: Kummer and Emmett showed an iron ammonia catalyst to be partially heterogeneous with respect to carbon monoxide adsorption[11] but not at all to nitrogen adsorption.[12]

This latter finding demonstrates the weakness in the differential isotope technique as applied, i.e. thermal desorption may result in migration of the adsorbate on the surface before desorption. Thus if the extreme assumption is made that all surfaces

are heterogeneous to some extent, measurements made by this technique will be measurements of the relative activation energies of migration and desorption for the species studied and only the most heterogeneous of surfaces will appear to be so. Cranstoun and Thomson[13] minimised the thermal effects by using mercury a more strongly adsorbed species, to displace hydrogen from a nickel film and proved this to be heterogeneous by the differential isotope technique using tritium as the labelled hydrogen. Toya[14] has recently demonstrated that all results from the differential isotope method may, at least qualitively, be explained on the basis of a homogeneous model.

In an attempt to remove as many of the conceivable causes of heterogeneity as possible, many recent studies have employed surfaces which can be prepared with a greater cleanliness than bulk adsorbents. Adsorption studies on such preparations as pure single crystals and high-vacuum deposited metal films have frequently shown a fast non-activated chemisorption not previously observed on the other catalyst forms.[15] Subsequent slow chemisorption led to the suggestion that many of the earlier studies involved adsorption on partially covered surfaces. Nevertheless techniques such as following the change of electrical resistance,[16] work

function[17] and sticking coefficient[18] have all demonstrated heterogeneity in the relatively uncontaminated films.

Field emission techniques have been used by Gomer,[19] Ehrlich[20] and Hansen[21] to show preferential adsorption on particular crystal faces, and the occurrence of different weakly and strongly bonded surface species on tungsten. The technique, reviewed by Gomer,[19] is however limited to the investigation of high index faces of highly refractory metals, although results obtained by Gardner and Hansen[22] on ethylene and acetylene adsorption, which are deduced to have occurred on different crystal faces of tungsten, will be discussed more fully below.

Early evidence of the geometric factor in catalysis was based on experiments on different adsorbents. It is highly unlikely that conditions of catalyst preparation and therefore crystallite size, surface cleanliness etc. could be exactly reproduced from one experiment to the next. Even if this were achieved different metals would certainly differ in more respects than the inter atomic distances on the surface exposed. In 1950 Rhodin[23] reported that the rate of oxidation of a single copper crystal was dependent upon the relative areas of the different faces exposed

and in 1958 Gwathmey and Cunningham[24] made a similar discovery for the rate of ethylene hydrogenation on a single crystal of nickel. Taken together with evidence from field emission studies, these results, while not achieved using the most modern methods of cleaning metal surfaces, confirm that an inherent heterogeneity of surfaces exposing more than one crystal plane will contribute to the poisoning and calorimetric effects detailed previously. The contribution to observations of heterogeneity of defects within a plane requires a technique capable of introducing or at least estimating the specific defect concentration on the surface and such studies are still in their infancy.[25]

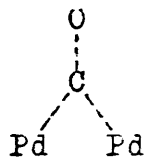
1.3 Heterogeneity of Surface Structures.

The heterogeneity of surfaces and hence of chemisorption on them may be reflected in the mode of adsorption of the gas i.e. different conditions of surface coverage or different faces of a single crystal may lead to distinctly different surface species. Many techniques for the investigation of the composition and/or the structure of the adsorbed species are well established. These techniques can be conveniently considered in three sections: (a) those in which the

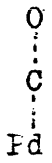
adsorbed species is observed directly; (b) those in which observations are made of modification in a property of the adsorbent which depends on the mode of adsorption; (c) calculation of the composition of the adsorbed species by observation of the composition of the reactant introduced and of the residual gas phase.

1.3.i Direct Observation.

The only widely applied example of (a) is infra-red spectroscopy and the published results are reviewed by Eischens and Pliskin (1958),[26] by Crawford (1960),[27] by Eischens (1964),[28] and by Little.[29] The classic demonstration of the power of infra-red spectroscopy as applied to surfaces was the discovery of the several surface species which exist when carbon monoxide is adsorbed on silica supported palladium,[26] two of which are identified as structures (a) and (b).



(a)



(b)

The latter predominates at high surface coverages.

Studies of hydrocarbon adsorption, in particular of ethylene, have been disappointingly inconclusive. Eischens and Pliskin[26] showed that ethylene chemisorption by silica supported nickel could either be

associative or dissociative depending on whether the surface was hydrogen covered or "clean". The composition of the dissociative residue was thought to depend on the degree of cleanliness of the surface with respect to hydrogen. Controlled hydrogenation of either adsorbate led to absorption bonds characteristic of C_2H_5 radicals. Acetylene chemisorption produced spectra similar to this, from which it was concluded that acetylene underwent self-hydrogenation on the clean nickel surface. Little, Sheppard and Yates[30] investigating ethylene and acetylene adsorption on silica supported palladium and nickel found similar evidence for associative and dissociative adsorption with the latter more pronounced on palladium. Hydrogenation gave rise to bonds which suggested polymerisation of the residual species from acetylene adsorption on palladium. Studies of hydrocarbon adsorption on alumina,[31] and alumina supported platinum[32] indicated that (a) on alumina where both acetylene and ethylene are adsorbed end on, the ethylene as ethyl radicals, adsorption of the acetylene and self hydrogenation of the ethylene take place on completely independent sites. (b) On platinum the same species are formed on ethylene adsorption. They are however more rapidly removed

on treatment with hydrogen at 100-150°C, with butane being observed in the gas phase.

Recent infra-red investigations by Morrow and Sheppard[33] of ethylene chemisorption on nickel and platinum confirm the results of Eischens and Pliskin on hydrogen covered catalysts but they do not observe the change of mode when adsorption is carried out on a clean surface. Spectra from adsorption on nickel were unstable both with respect to time and temperature and high yields of butane on hydrogenation indicated that slow polymerisation on the surface might be the cause.

1.3.ii Indirect Physical Techniques.

Techniques relying on the modification of the adsorbent surface, type (b), are by their nature less directly informative than infra-red spectroscopy, the principal result being the number of bonds existing between the adsorbate and the surface. Results of hydrocarbon chemisorption from three such methods, electrical conductivity of films,[34] magnetisation of supported catalysts,[35] and field emission microscopy using single crystals[19] will be considered.

The electrical conductivity of metal films is affected by the "loss" of electrons into covalent bonds with the chemisorbed species. By assuming a

one electron "loss" for each hydrogen atom chemisorbed, an apparatus can be calibrated and subsequently used to determine the number of bonds between an adsorbed molecule and the surface. Zwietering, Koks and van Heerden,[36] using this technique in the study of chemisorption, report multi-site attachment for ethylene on a titanium film until approximately half coverage, after which there is a fall in the number of bonds to the surface. The former is probably the dissociative mode occurring on the clean surface but the inability of the technique to distinguish between carbon and hydrogen bonds to the surface made all deductions tenuous without supporting evidence from other methods.

Selwood has studied the change in magnetisation of nickel on the adsorption of various molecules and, by a calibration technique similar to that described for electrical conductivity, can evaluate the number of surface bonds to each chemisorbed species. Chemisorption of ethylene and ethane on a nickel/silica catalyst[37] was studied and by supplementing the magnetisation information by gas phase analysis, the following deductions were made:

(a) at low temperatures ($\sim 0^{\circ}C$) adsorption was associative and self-hydrogenation negligible.

(b) at higher temperatures ($100^{\circ}C$) adsorption

(b)/ was dissociative, self hydrogenation significant, and, if the ethane produced was removed, the adsorption capacity of the catalyst for ethylene was greatly increased.

(c) ethane at room temperature, since chemisorption necessitates dissociation, involves more surface bonds than ethylene.

The use of the field emission microscope as a technique for observing chemisorption of hydrocarbons has, as yet, been limited. Hydrocarbon adsorption has been confined to that on tungsten and iridium. Tret'yakov[38] in 1960 observed the adsorption on a tungsten single crystal of ethylene, propylene and acetylene. Interpretation at that time was difficult but adsorption of each hydrocarbon appeared to take place on two sites; the site spacings were independent of the hydrocarbon studied and all of them left a carbon film on the crystal. More recent work on the same system by Gardner and Hansen,[22] studying ethylene and acetylene adsorption from 4 to 1000°K indicated that acetylene below 300°K and ethylene below 200°K were associatively bonded. At 200-300°K ethylene dissociated to an acetylene species and hydrogen, and at higher temperatures adsorption resulted in carbon

deposition from both hydrocarbons. An argument for the adsorption of ethylene and acetylene taking place on different crystal planes is put forward. In earlier work (1962) on iridium, Arthur and Hansen[39] demonstrated the increasing tendency to dissociative adsorption of ethane, ethylene and acetylene with increasing temperature, finally resulting in a crystallisation of the carbon residue.

1.3.iii Indirect Chemical Techniques.

Long before the advent of the sophisticated techniques of type (a) and (b) investigations, the existence of differently bonded and relatively active and inactive adsorbates had been detected by standard methods of following gas reactions and by analysis. Findings of this work were frequently substantiated by later deuterium and carbon - 14 tracer and exchange techniques. A summary of the results of some of these investigations is given below with a particular emphasis on the identification of the strongly bonded residues from the adsorption of C_1-C_3 hydrocarbons. The summary cannot pretend to be exhaustive, because of the fact that many observations of "irreversibly adsorbed small fractions", for example, are to be found as asides and comments in papers on other work.

Ever since the early reference of Sabatier[41] to the apparent carbonisation of a nickel catalyst, residues have frequently been invoked to explain either the poisoning of a catalyst reaction or the extent of exchange in an exchange reaction. In 1936 Morikawa, Benedict and Taylor[41] postulated dissociative adsorption of methane on an active nickel catalyst at temperatures $> 140^{o}C$ and in a later re-examination of the system using methane-d^4 Wright and Taylor[42] confirmed the existence on the surface of all possible fragments from CH_4 to C. Similar studies with ethane[43] and propane[44] showed dissociation by C-H bond fission and hydrogen exchange at $< 130^{o}C$ and by C-C bond fission to produce methane at higher temperatures. At $0^{o}C$ ethylene was observed to polymerise on the nickel catalyst[44] but breaking of the C-C bond was negligible. Polymeric residual species were also postulated on the basis of the other type of observation i.e. self-poisoning. Pauw and Jungers[45] and later Tamaru[46] found evidence of poisoning of acetylene hydrogenation on nickel and palladium respectively and ascribed it to the formation of polymers on the surface. Regeneration of the nickel catalyst was possible by hydrogen treatment at $300^{o}C$.

Once the existence of active and inactive ad-

-sorption had been established by exchange and poisoning of hydrogenation reactions, many investigations were carried out to study the products, gaseous and residual, of the adsorption of one gas rather than a reaction mixture. A summary of the more well-documented results is given below for various hydrocarbons.

Methane.

In a very simple experiment on a alumina-supported nickel catalyst at 150-200°C Troesch[47] showed that in the absence of hydrogen, methane was adsorbed such that some of it could be considered to have reacted thus:

$$3\ Ni + CH_4 = Ni_3C + 2H_2$$

As a result of a later experiment[48] he favoured a hydrogen deficient residue theory rather than the formation of nickel carbide. In 1956 Trapnell,[49] in an extensive investigation, noted that methane was adsorbed by vacuum evaporated films of palladium and rhodium though not of nickel. Adsorption increased with rising temperature but no poisoning or hydrogen desorption occurred in the range studied, -78 to 70°C. 1958 saw the beginning of a semiquantitative estimation of the composition of the methane residue by Wright, Ashmore, and Kemball.[50] At temperatures > 100°C adsorption of methane on films of tungsten, iron and

nickel led to hydrogen formation and surface residues which were calculated to be of average composition $CH_{0\rightarrow 1}$ on nickel and CH_2 on iron both at 200°C. Roberts[51] in 1963, using ultra high vacuum (5×10^{-9} torr) conditions for the preparation of his films found adsorption but no decomposition of methane on iridium films at 27 and 100°C.

Ethane.

In the same paper and therefore under the same conditions as above, Trapnell[49] reported a study of the adsorption of ethane on several metal films. Although adsorption was observed on several films including rhodium and palladium, decomposition with evolution of hydrogen was observed only for tungsten, molybdenum, and rhodium at > 0°C, and residual species were calculated at $C_2H_{4.8}$, $C_2H_{5.8}$ and $C_2H_{3.9}$ respectively. In 1958 Wright, Ashmore, and Kemball[50] reported that adsorption of ethane on films followed by heating to > 100°C for three hours resulted in the formation of residues of composition C_2H_2, C_2H_4, and C_2H_5 for tungsten, nickel and iron respectively. Roberts[51,52], carried out studies of ethane adsorption on UHV prepared films of rhodium and iridium. He observed that adsorption led to decomposition at 0°C, residues from adsorption at 100°C were of composition $CH_{1.5}$ for rhodium and

$CH_{2.5}$ for iridium, and that monocarbon fragments only were present on the surface at 100°C. Roberts has reviewed his work to 1963.[53]

Propane.

In a study of the adsorption residues of propane Roberts[54] notes that at 27°C on a rhodium film hydrogen, methane, ethane and a residue composition of $CH_{2.5}$ were obtained. At 100°C methane was the main product and the residue composition was $CH_{1.7}$. McKee[55] (1962) investigating propane cracking over nickel in the range 100 to 200°C, found propane cracked at a lower temperature than ethane and that the main product was methane leaving a residue of average composition $CH_{1.6}$. Similar results were obtained over platinum[56] where the residue composition was again $CH_{1.6}$.

Hydrocracking of Alkanes.

The kinetics of the hydrocracking of ethane[57] have been studied and a mechanism postulated in which the rate determining step is considered to be the reaction of a residue with adsorbed hydrogen. No attempt was made to estimate the composition of the residue. Later Anderson and Baker,[58] investigating the hydrocracking of gaseous hydrocarbons over films of nickel, rhodium, tungsten and platinum, observed that at temperatures just below the range for hydrocracking (150-200°C)

adsorption involving carbon-carbon bond rupture was rapid and coverage by residues was approximately 50%. For ethane and propane residue composition ranged from $CH_{0.4}$ to CH_2. Demethanation and hydrogenolysis of cyclopropane (McKee[59]) were found to proceed simultaneously on platinum, the products being methane, ethane and propane and a surface residue of average composition $CH_{1.1}$ cf $CH_{1.6}$ of propane. Knor et al.[60] studying chemisorption and hydrogenation of cyclopropane on a nickel catalyst observed extensive cracking in the absence of hydrogen and Taylor, Yates and Sinfelt[61] investigating the hydrogenation over supported nickel concluded that the production of C_1 and C_2 species was much faster from cyclopropane than from propane.

Ethylene.

The hydrogenation of ethylene is the most thoroughly investigated reaction of its kind[62,63] and consequently its adsorption and residual species are also widely reported. General conclusions only are summarised below and references given to support these are shown at the appropriate places. The self hydrogenation of ethylene in the absence of hydrogen, leaving hydrogen deficient residues of the surface is well established for a number of catalyst preparations.[64,65,66] General characteristics

of the reaction are -

(1) it only begins to take place at high coverages.[64]

(2) polymerisation is indicated by production of butane.[64]

(3) at temperatures above that for hydrogenation to ethane, methane is recovered.[65]

(4) the reaction on nickel is retarded by pre-adsorbed acetylene.[66]

Propylene.

In addition to the associative mechanism of adsorption considered to be the intermediate in propylene hydrogenation, evidence is presented for a hydrogen deficient residue on palladium powders.[67]

Acetylene.

There is little reported work on the adsorption of acetylene in the absence of hydrogen.[68] Trapnell (1953)[69] showed that it occurred on a greater diversity of evaporated films than did ethylene.

Hydrogenation of Unsaturated Hydrocarbons.

As stated previously the existence of residues is frequently only mentioned in passing in many hydrogenation studies, the main interest being in the active adsorption. Summarised in this section are some of the main references

to self poisoning residual species etc.

The early investigations of acetylene hydrogenation self-poisoning by Jungers[45] (1948) and Tamaru[46] (1950) have been cited earlier. Beeck[70] in 1950 studied the rate of hydrogenation of ethylene over various films and found that irreversible poisoning by acetylenic residues formed by self - hydrogenation rendered the surface inactive for hydrogenation. The composition of the residue had a limiting value of $CH_{0.4}$ and polymerisation was also shown to have taken place on the surface. Sheridan and Reid[71] noted that over rhodium hydrogenation of acetylene produces partially hydrogenated polymers to an extent of approximately 20%. Jenkins and Rideal[72] who investigated the chemisorption of ethylene prior to hydrogenation considered it to have been dissociatively adsorbed and heating to 170°C to have removed the chemisorbed hydrogen so produced. Tuul and Farnsworth[73] investigating the poisoning of a single crystal nickel catalyst for the hydrogenation of ethylene concluded that at temperatures greater than 175°C the surface rapidly became covered with adsorbed fragments of hydrocarbon.

From the above examples and the evidence presented in earlier sections of this introduction it is

apparent that catalysts no matter how prepared, are capable of adsorbing hydrocarbons in several modes. That only some of these are active in hydrogenation has also been demonstrated. An isotope technique for measuring the relative amounts of active and inactive chemisorption under reaction conditions was first applied to hydrocarbon hydrogenation by Thomson and Wishlade[74] when they found that inactive adsorption of ethylene on a nickel film was 11 to 47% of the total chemisorption. This investigation was later extended to a series of alumina supported catalysts[75] when inactive adsorption of ethylene to the extent shown below was observed.

Pd	Ni	Rh	Ir	Pt
63.5	24.0	22.5	16	6.5

CHAPTER TWO

THE AIMS OF THE PRESENT WORK

Throughout the literature there are many papers describing adsorption, residual species etc. (Chapter 1). Investigations which are wide in scope are few,[69,70] and although deductions on the nature of the adsorption are made, this is seldom done under catalytic reaction conditions. Comparisons between one report and another are frequently of little use owing to differences in catalyst preparation, experimental conditions and procedure. Thus it was decided to build on the information already available[75] by using alumina-supported catalysts and thereby to obtain a considerable volume of information about retention on these catalysts.

The investigations described herein were undertaken to determine the causes of the difference in reactivity of the two fractions of ethylene adsorbed on a catalyst as evidenced by the previous work in the laboratory.[74,75] This has been attempted before but the only variable against which the retention has been measured was that of the catalyst metal and the results were inconclusive.[75]

Consideration was now given to the most likely sources of further information. Infra-red spectroscopy and the other physical methods described in section 1.3. could not be applied to the powdered alumina

catalysts. Since the difference observed was one of reactivity it was decided to pursue this line of study by employing radioactivity methods to determine the proportion of adsorption which was reactive and the dependence of this proportion on various parameters.

When a molecule is considered to be capable of adsorbing by both an associative and a dissociative mechanism the latter is observed to predominate at higher temperatures.[33,37] Hence if reactivity is a function of the mode of adsorption then differences should become apparent by studying the proportion of reactive to unreactive adsorption at various temperatures. Further evidence for a dependence of this nature should be gained from a study of the adsorption of various hydrocarbons of different degrees of unsaturation. Information from such experiments might also indicate a geometric effect. If unreactive and reactive adsorption were a function of crystal face, and the hydrocarbons used had bonds of different lengths, then preferential adsorption on different exposed faces might be expected.

In addition to studying the variation in retention, it was thought that the properties of the residue might be investigated, particularly with reference to

their reactivity with acetylene which has been postulated as affecting the retention markedly.[75]

In conclusion, then, the aim of the work is to identify the surface species corresponding to reactive and unreactive fractions of hydrocarbons adsorbed on alumina-supported catalysts by investigating,

(1) the variation of the relative amounts of each with temperature,

(2) the variation of the relative amounts of each with different hydrocarbons,

and (3) the reactivity of the "unreactive" fraction with other species.

To these ends it was considered necessary that chemical analyses of the reactants introduced and products desorbed be undertaken in addition to the observations made previously.

CHAPTER THREE

APPARATUS AND EXPERIMENTAL PROCEDURE

3.1 Introduction.

The radiochemical study of adsorbed species is a highly satisfactory and well established method of measuring the amounts of a particular radioisotope on the surface. It has the disadvantage, however, that information cannot be obtained concerning the chemical form of the adsorbed species. This can be determined by spectroscopic methods but it would be difficult to combine these with radio-activity measurements.

For the present investigation it was decided to use a subtractive technique to obtain information on adsorption and adsorbed species. By this method the C:H ratio of the surface residues can be deduced from a knowledge of the reactants used and the species desorbed from the surface. Gas chromatography was an obvious choice for such analysis.

Two reaction systems were considered. One was a static high-vacuum system in which reactants could interact with a catalyst and the products be subsequently analysed. The second was a flow system, comprised of a microcatalytic reactor coupled directly to a chromatographic column. The flow system had the ad-

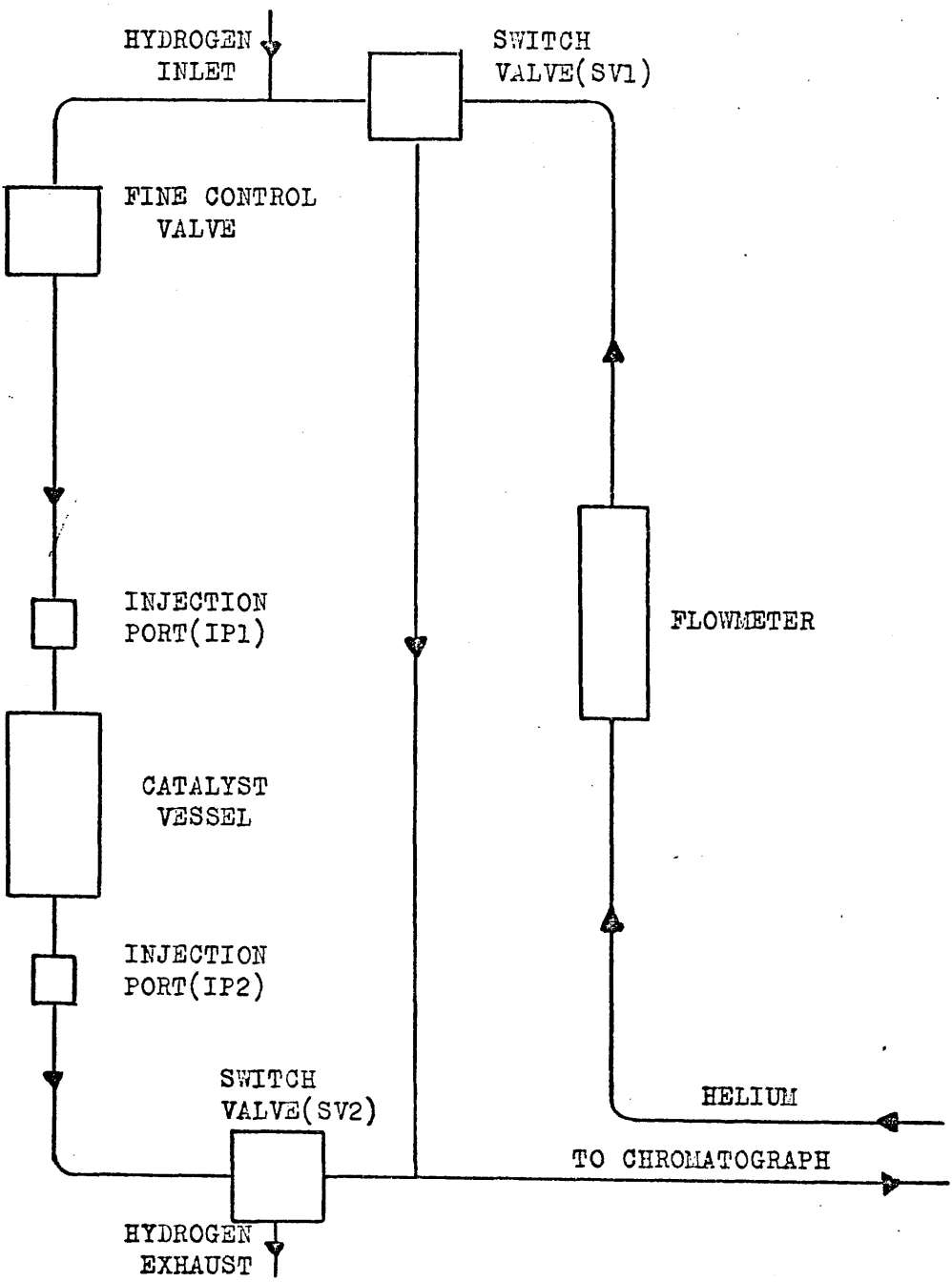


Figure 2. Flow Diagram of the Catalyst Section.

-vantage of flexibility of reactant dosing and speed of analysis. Combined, however, with the requirements for the measurement of adsorption over a wide range of temperature, it precluded direct monitoring of the catalyst with a Geiger counter: this had been done at 25°C and 60°C by previous workers in the laboratory.

Radioactive tracers had, therefore, to be used in a different way. If they were to be injected into a flow system their fates could best be followed by monitoring the gases emerging from the chromatographic column. This, by a subtractive procedure, would yield the amounts of activity retained by the catalysts. There was also the possibility that when residues were removed from the catalysts by various treatments, chromatography and the measurement of radio-activity would give information on the chemical form of the desorbed species. This information could not be obtained from direct radiochemical observation of the surface.

A block diagram of the flow system, which is similar to that described by Kokes, Tobin and Emmett[76] is shown, together with the associated instrumentation in figure 1.

3.2 The Catalytic Reactor and Chromatograph.

Minor alterations had to be made to the Beckman GC2A chromatograph which was to be used in this study. The gas and liquid sampling inlets provided were removed and replaced by the catalyst section of figure 1. The resultant increase in the gas flow resistance necessitated the removal of the capillary restrictor, located in the sample line, in order to keep the flow rates in this and the reference line approximately equal.

The detailed construction of the catalyst section is shown in figure 2. The sample line of the chromatograph, $\frac{1}{8}$" o.d. tubing, is led out immediately after the capillary block to a vertically mounted board where it is sealed with "Araldite" into a "Rotameter" gas flowmeter. This was calibrated in isolation and in situ against a soap-bubble flowmeter at the end of the system. Correlation of these calibration curves indicated that no leaks were present in the system. The "Rotameter" was thereafter used to indicate the flow rate of the carrier gas before blending, at the chromatograph exit, to form a counting mixture (figure 1 and section 3.6). From the flowmeter the line entered a rotary switch valve SV1 (Drallim Industries Ltd.) where if necessary the carrier gas could be led

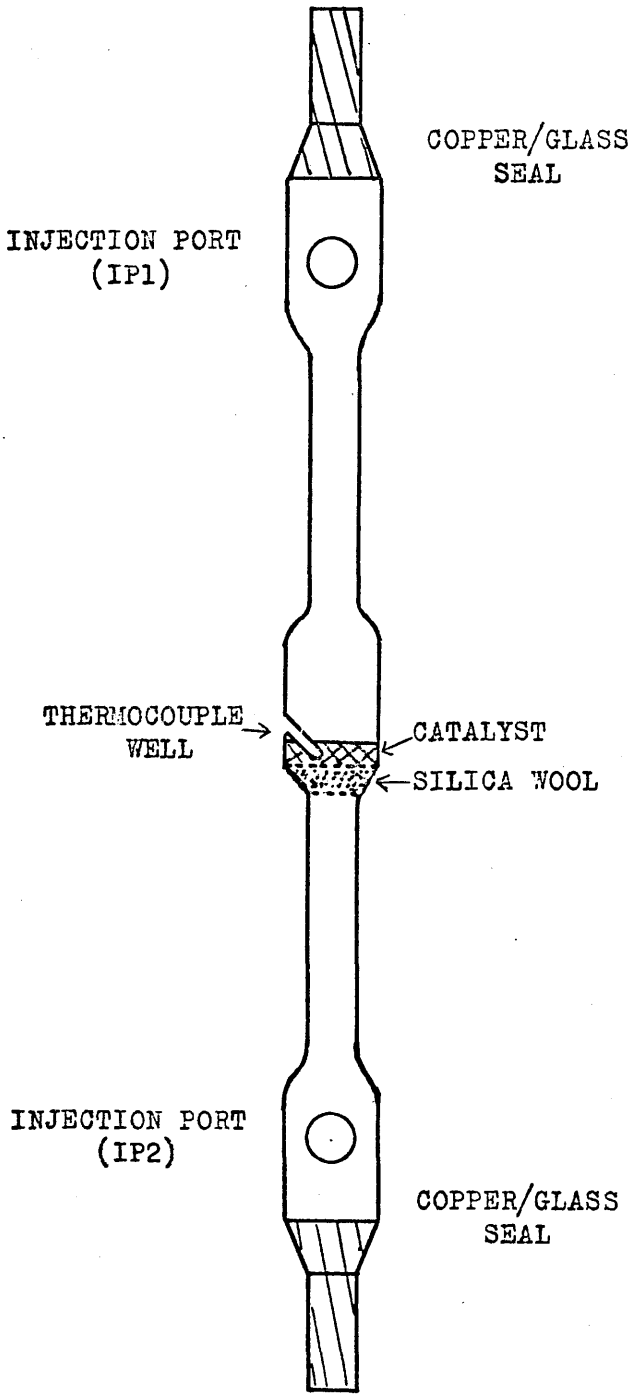


Figure 3. The Catalyst Vessel.

directly back to the chromatograph; the junction with the chromatograph was immediately before the column. This will be referred to as the catalyst by-pass circuit.

With SV1 in its alternative position the carrier gas flow was directed first through a "Nupro" fine control valve, used to balance flow rates in the sample and reference lines, and then into the catalyst vessel. (figure 3). The catalyst vessel was made of "Pyrex" glass with a copper - "Pyrex" seal at each end to make joints to the otherwise all metal system. The design of the vessel was the result of experiment in which both wide (15 mm.) and narrow (7 mm.) bore tubing were used. The pipette-shaped final design kept the dead volume of the vessel to a minimum but permitted quantities of catalyst up to one gram to be used without the catalyst bed itself acting significantly as a chromatographic column. Injection ports IP1 and IP2 for reaction and calibration injections respectively were situated 6cm. above and below the catalyst bulb. The diameter of these ports was such that a tight seal was obtained with the $\frac{1}{4}$" serum caps ("Subaseal") which had both internal and external sealing edges.

The return of the gas line to the chromatograph was made through a second switch valve (SV2) and a T-piece fitted with diaphram metal taps to prevent

surges of gas when the switch valves were turned. This T-piece which made the join of the by-pass circuit and the main line, was a "Crawford Swagelock" fitting, as were all the other couplings on the system. The provision of SV2 was to permit exhaust to atmosphere of hydrogen, which entered the section through a T-piece after SV1, and was used for the in situ reduction of the catalysts. During these reduction periods, the conditions of which are fully described in section 3.8., the carrier gas stream flowed continuously through the rest of the system via the catalyst by-pass circuit.

The temperature of the catalyst could be raised by a cylindrical electric furnace surrounding the catalyst vessel. The current to the furnace was controlled via a "Variac" variable transformer and the temperature of the catalyst was measured using a platinum/platinum-rhodium thermocouple. A calibration curve, determined experimentally, allowed a correction for the temperature gradient between the outside and the inside of the vessel when gas was passing through it at various rates.

3.3 The Sample Preparation Apparatus.

In order to prepare reactant gases for transfer into the flow system, by syringe injection, a vacuum

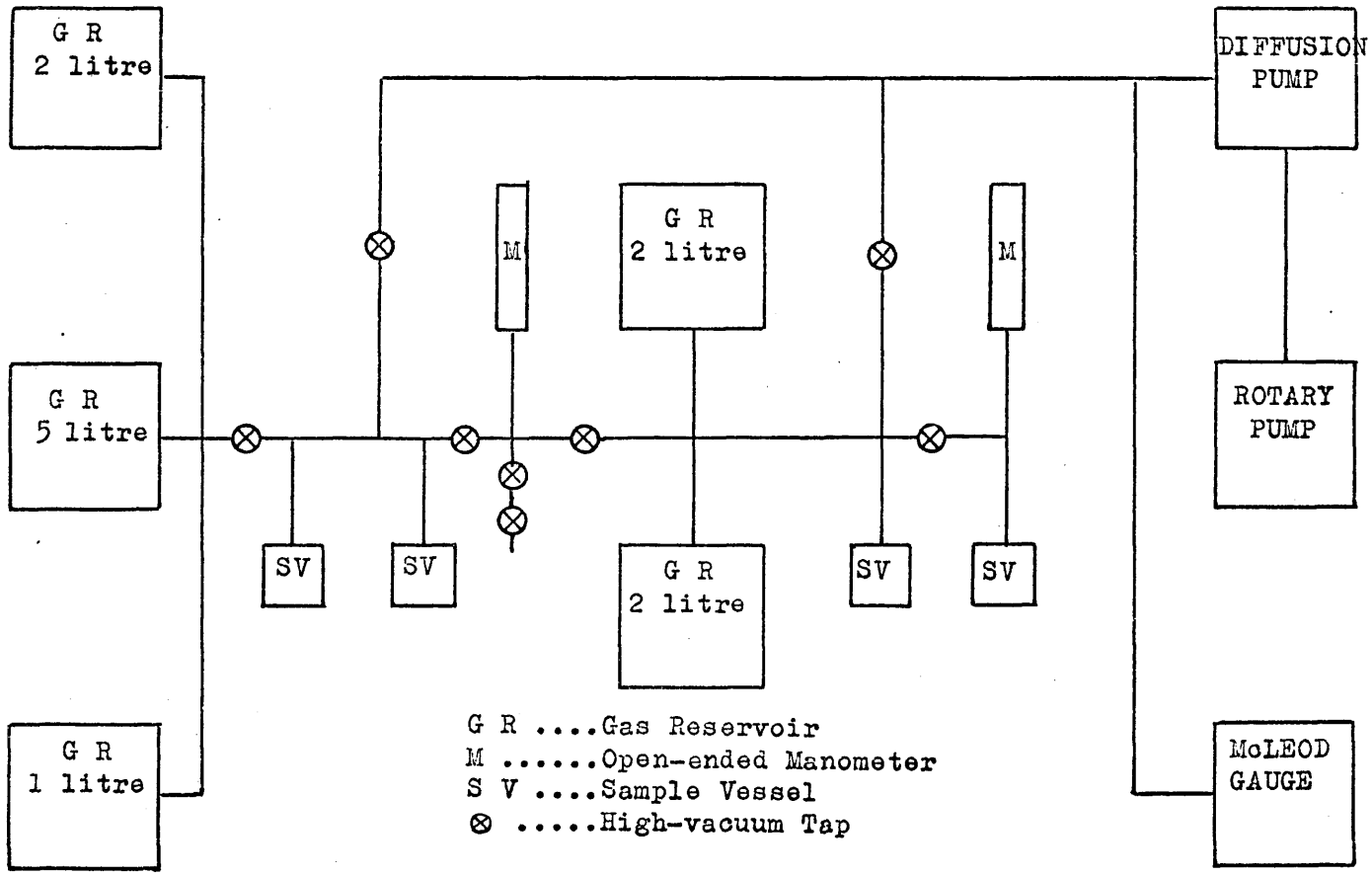


Figure 4. Block Diagram of the Sample Preparation Apparatus.

apparatus was constructed (figure 4). The necessary design features included facilities for storing several gases, purification by fractionation, and transfer of gases to sample vessels at measured pressures greater than atmospheric.

The pumping system for the apparatus was conventional, i.e. a diffusion pump backed by a rotary one, with taps and traps to isolate and protect the diffusion pump when necessary. Two connections were made from the main (20 mm.) line to a secondary manifold (12 mm.). This was divided as shown by 2 mm. taps and had connected to it, five gas reservoirs (GR) of various capacities, four sample vessels (SV) of $\sim$ 60 ml. fitted with injection ports and serum caps, two open ended capillary manometers, and a doubly tapped outlet to atmosphere, used to fill reservoirs with reactant gases from cylinders. As well as those shown all vessels and reservoirs had 2 mm. taps which together with all other taps and glass joints were lubricated with "Apiezon N" vacuum grease.

In addition to the mercury manometers, an "Edwards Vacustat" (range 1 to 10^{-3}torr) and a McLeod gauge were fitted to the system. The capillaries of the McLeod were of Jencons Ltd. 1 mm. precision bore tubing and the volumeof the bulb (140.5_2ml.) was such

that pressures of 10^{-2} to 10^{-5}torr could be measured. Both calibrated gauges were used to determine the residual pressure (a) in the evacuated system and (b) over condensed gases.

The transfer of gases from the preparation apparatus to the flow system was effected by "Hamilton Gas Tight" syringes. Details of their performance are discussed in section 3.5. Calibration Procedure.

3.4 Materials.

(a) The catalysts, supplied by Johnson Matthey & Co. Ltd., were 5% impregnations on α - alumina of palladium, rhodium and platinum. The surface area per gram was approximately the same for all three catalysts but the metal surface areas, determined by CO adsorption at Johnson Matthey, differed markedly (Table 1).

TABLE 1.

Catalyst Surface Areas.

	Total Surface Area (m^2g^{-1})	Metal Surface Area (m^2g^{-1})
Palladium	111	5.0
Rhodium	141	0.8
Platinum	147	0.2

(b) Careful consideration was given to the choice of carrier gas to be used in the system. The possibilities were hydrogen, helium, nitrogen and argon. The use of hydrogen would preclude observation of adsorption in anything other than total hydrogenation conditions. The use of helium would make accurate quantitative measurement of hydrogen injections difficult and under some conditions impossible. This is due to the dependence of the chromatograph detector on thermal conductivity and the similarity of this property of the two gases. (Table 2).

TABLE 2.

Thermal Conductivity of Various Gases.

Gas	Thermal Conductivity*
Hydrogen	39.60
Helium	33.60
Methane	7.20
Nitrogen	5.68
Ethane	4.31
Argon	3.88

* Thermal conductivity in g-cal.sec.$^{-1}$cm.$^{-2}$/^{o}C cm.$^{-1}$ at 0^{o}C from Lange's Handbook of Chemistry.

This similarity gives rise to a very low sensitivity and under certain concentration conditions an inverted output response. The thermal conductivities of nitrogen and argon are such that the system would have very low sensitivity for hydrocarbons and different components of one analysis may have output responses in different senses. The accurate estimation of the hydrocarbons eluted was considered to be more important than that of hydrogen, and helium was accordingly chosen as the carrier gas.

The comparison of results obtained before and after the insertion into the gas line of a 5A molecular seive trap, maintained at - 195°C, indicated that the helium contained no significant amount of impurity which would affect the catalyst. The trap was, however, always used lest the helium purity varied from cylinder to cylinder. The helium was obtained frim Fisons Ltd., who supplied the following analysis figures:-

Helium	99.995%
Oxygen	1 - 10 ppm.
Nitrogen	1 - 20 "
Moisture	2 - 10 "
Neon	5 - 20 "
Methane	0.3 - 2 "
Hydrogen	0 - 2 "
Argon	1 "

Hydrogen, used in the reduction/activation of the catalyst was obtained from the British Oxygen Co. Ltd. This was passed through an "Engelhard Deoxo Hydrogen Purifier" which had the effect of lowering any oxygen impurity to less than 1 p.p.m. by conversion to water vapour. That it did not require periodic regeneration suggested that the purifier did not retain the vapour produced. A 5A molecular seive trap maintained at -195°C was therefore inserted in this line. Both molecular seive traps were regularly baked out under vacuum at $\sim$ 100°C.

Methane, used to form a counting mixture with the helium, was the "CP grade" of Air Products Ltd., who quote the purity as greater than 99%, nitrogen, at less than 0.77% being the principal impurity. Since this gas did not pass over the catalyst its purity was less critical and it was used as supplied.

(c) Reactant gases were obtained as follows:-

Hydrogen and Methane as above,
Ethylene, Acetylene and Cyclopropane
from British Oxygen Co. Ltd.,
Ethane, Propane, Propylene, and
But-1-ene from the Matheson Company.

The hydrocarbons, received in various degrees of purity, were repurified by condensing and degassing followed by

fractional distillation; the high and low boiling fractions being rejected. Methane which has a vapour pressure of 10 torr at liquid nitrogen temperature could not be degassed as thoroughly as the others, but the fractionation technique was successful in purification to within the limits required. The purity of all samples was determined by the syringe sampling technique and when contamination was observed in an injection to an extent of greater than 0.5% the sample was rejected and the gas repurified. When an impurity of less than 0.5% was observed (this was most frequently air) its appearance was noted but the experiment continued.

Hydrogen, purified as detailed in (b) was admitted after initial evacuation to the section of the apparatus in which it was to be stored. The section was then pumped down to less than 10^{-5} torr and subsequently refilled.

3.5 Calibration Procedure for the Chromatograph.

Accurate quantitative analysis by gas chromatography depends on,

(1) Sampling Technique,

(2) Chromatograph Performance,

(3) Recorder Characteristics,

and (4) Human Factors, ranging from skill in

introducing the sample through to evaluation of the data obtained.

The sampling technique chosen to give the greatest flexibility for the present problem was to introduce reactant gases by "Hamilton Gas Tight" syringes fitted with "Chaney Adaptors". These instruments could be set ± 2% at mid-scale but with the adaptor a reproducibility of the injection size of 0.01% is claimed. By using syringes of 0.25, 1.0, 2.0 and 10.0 ml. capacity it was thus possible to inject any quantity of gas from 0.02 to 10 ml. with a very high degree of reproducibility.

Chromatograph response was optimised as far as the system would permit. The special problems of a microcatalytic reactor are that long elution times and hence temperature programming of the column are not possible if several injections are to be made under similar catalyst conditions. This made simultaneous analysis of mixtures of a wide range of components impossible. Thus, e.g., in experiments with acetylene, the resolution of hydrogen, methane and air, if present, could not be achieved simultaneously with an accurate estimation of ethylene and acetylene. The individual chromatography conditions for each type of analysis are described later in this section

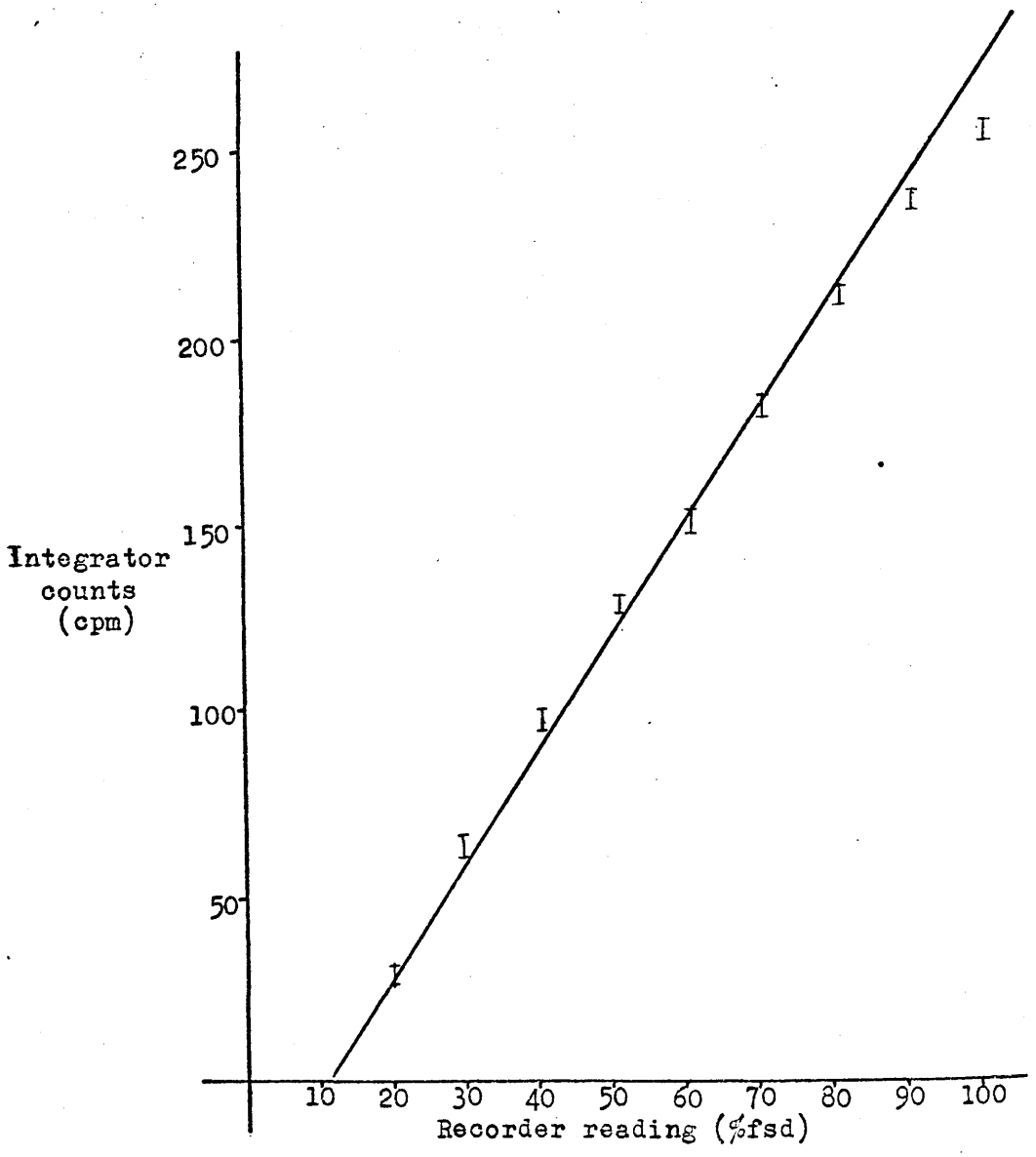


Figure 5. Integrator Calibration.

together with the calibration data.

Initially a Honeywell 0-1mV recorder was used and quantitative results were obtained by computing the area of the peaks obtained using an "Allbrit" fixed arm planimeter. It was soon realised that experiments could be completed as accurately, with no significant loss in sensitivity, but much more quickly by replacing this recorder by a Honeywell -0.25 to 2.5mV recorder fitted with an electro-mechanical continuous integrator unit. The integrator was not perfectly linear in response throughout the range of the recorder, deviations being greatest at outputs less than 2% f.s.d. From deflections of 2% to 90% of full scale, however, the count rate as shown in figure 5, corresponded to a linear relationship of 108 ± 5 counts per mV.min. This is probably in considerable excess of any other error in recorder instrumentation but is about the same as that made in measuring by planimeter the large number of peaks from each experiment. The quoted deviation from linearity does not affect the accuracy of the calibration system which is detailed below.

The skill of the operator is probably the factor which determines the precision in this application of chromatography. The particular applications which were

most susceptible to this, were the reactant dosing and the integration of the recorder trace.

Reactant dosing consisted of removing a quantity of gas from a vessel, in which it was maintained above atmospheric pressure, and injecting it into the helium stream either above or below the catalyst bed. During the transference, some of the gas expanded out of the syringe leaving the desired volume at atmospheric pressure. Two sources of error in this operation, proposed to explain the occasional larger than instrumental deviation, were the partial blocking of the needle and too fast a rate of injection. The former, depending on the stage of the operation at which it occurred, resulted in injections of hydrocarbon at pressures lower or higher than atmospheric: the latter caused a temporary leak in the self-sealing serum cap and resulted in a loss of hydrocarbon.

The need for being skilled in integrating the recorder trace arose from the fact that the integrator is continuous and must be read and/or zeroed before and after every peak. Deciding where peaks began and ended was particularly difficult under two sets of conditions: when the catalyst bed was maintained at room temperature a greater degree of peak 'tailing' was observed and this obscured the end of the peak:

and secondly when resolution of components of short retention time was necessarily poor to facilitate total analysis in the desirable time. Under both these conditions the accurate estimation of small peak areas by integrator was impossible and the planimeter was frequently used to improve the precision of the measurement.

In order to eliminate errors due to day to day fluctuations in ambient and instrumental conditions, a calibration was incorporated in every experiment. If the experiment was particularly long it was repeated at frequent intervals. The calibration usually consisted of a number of replicate injections of the initial reactant dose from which the sensitivity of the chromatograph was calculated. This was related to a complete calibration table which was the result of an experiment under identical conditions. In this, a range of injections of the reactant and all possible products was made and the sensitivity of each component related to the reactant. Linearity between successive points on the calibration curves was assumed after investigation showed that it introduced no significant error. The conditions for each set of analyses together with the relevant calibration table are shown below.

For all, except C_4 hydrocarbon analyses, a 10 ft. long, $\frac{1}{4}$" o.d. stainless steel column fitted with 30-60 mesh silica gel (Perkin Elmer Ltd.) was used. The chromatograph was operated with a helium flow rate of 60ml.min^{-1} and a filament current of 200mA.

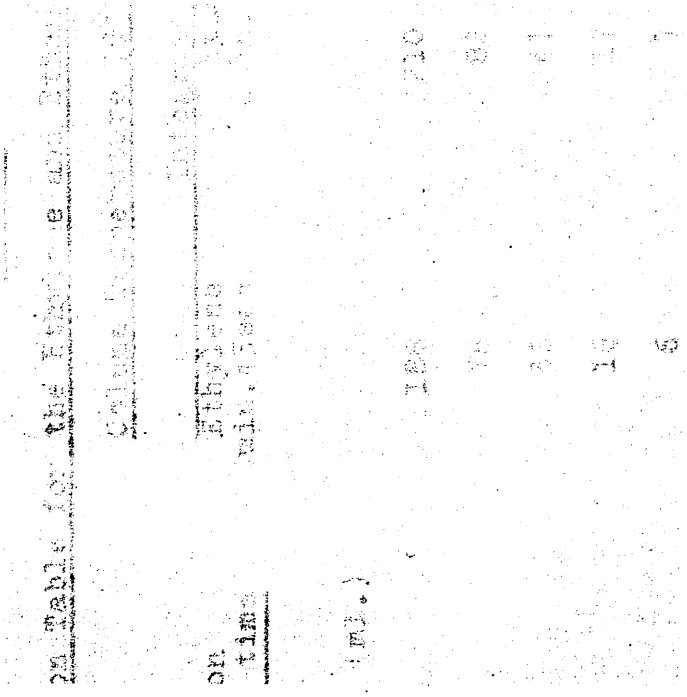


TABLE 3

Calibration Table for the Ethylene and Ethane Adsorption Experiments.

Column Temperature 70°C.

hydrocarbon retention time	Integrator Counts Ethylene 4min.45sec.	Ethane 2min.45sec.	Methane 1min.30sec.
volume of injection (ml.)			
0.5	188	210 (.89)	
0.2	78	82 (.95)	
0.1	36	41 (.88)	26 (1.38)
0.05	16	17 (.94)	13 (1.23)
0.025	6	7 (.86)	-
0.01	1.5	2 (.75)	2 (.75)

TABLE 4

Calibration Table for the Acetylene Adsorption Experiments.

Column Temperature 130°C.

hydrocarbon retention time	Integrator Counts Acetylene 3min.40sec.	Ethylene 2min.10sec.	Ethane 1min.50sec.	Methane 1min.25sec.
volume of injection (ml.)				
0.5	162	188 (.86)	-	-
0.4	129	140 (.92)	-	-
0.3	86	102 (.84)	-	-
0.2	57	70 (.82)	-	-
0.1	26	33 (.79)	36 (.72)	25 (1.00)
0.05	12.5	16 (.78)	17 (.74)	14.5(0.86)
0.025	5.5	7 (.78)	7.5(.74)	5 (1.1)
0.01	-	2 (.79)	2	

TABLE 5

Calibration Table for C_3 Hydrocarbon Adsorption Experiments.

Column Temperature 130°C.

hydrocarbon retention time	Integrator Counts				
	Propylene 5min.	Cyclopropane 4min.	Propane 3min.	Ethane 2min.10sec.	Methane 1min.30sec.
volume of injection (ml.)					
0.5	81	74	74	59	41
0.1	13	11	12	10	8

In tables 3 and 4 the sensitivities shown are all converted to the same instrument attenuation 5. In table 5 the sensitivities were measured and are quoted at instrument attenuation 20.

In tables 3 and 4 the figure in parenthesis is a relative sensitivity to the reactant which was used, in conjunction with the reactant calibration of a particular experiment, to obtain the exact product sensitivities in that experiment. In table 3 it is calculated relative to ethylene and is averaged, taking account of the observed yields, at 0.9 for ethane and 1.0 for methane. In table 4 it is calculated relative to acetylene and is averaged at 0.80, 0.74 and 1.0 for ethylene, ethane and methane respectively.

From table 5 relative sensitivity factors taking account of the observed yields in experiments were as follows:-

	Propylene	Propane	Ethane	Methane
to cyclopropane	0.9	1.0	1.1	1.4
to propylene	1	1.1	1.3	1.6

For several other less extensive investigations, methane adsorption, but-1-ene adsorption, and purity investigations, no detailed calibration procedure was adopted and experimental conditions and calibrations

will be given together with the results.

3.6 Counter Design.

Having decided to employ a subtractive method of estimating the radioactive species retained on the surface a counting system had to be chosen which could efficiently detect radioactivity in the gases eluted from the chromatograph. From reviews by Adloff[77] and Cacace[78] on this subject the following information was obtained. (Table 6). Since it was possible that tritium might be used in the study, it was concluded, on the grounds of counting efficiency, that an internal gas flow counter should be used: a proportional counter was selected in preference to an ionisation chamber for the reason given in the above table and because of advantages at low level counting. In the case of the ionisation chamber, under such conditions, either a large resistor must be used with the associated electrometer or the rate of charge method must be used. The latter method cannot be applied where the activity is varying as it is in a flow system, and the former introduces a large time constant which will aggravate any component separation difficulties.

A proportional flow counter to the design of Schmidt Bleek and Rowland[79] was constructed with minor alterations to accommodate different connectors both for the gas inlet and high voltage supply. The

TABLE 6

Radioactivity Detectors for Analysis of Chromatograph Eluants.

Detector	Approximate Efficiencies		Other Information
	C^{14}	H^3	
Geiger (Thin Window)	10%	0	-
Proportional (Flow)	100%	100%	Involves critical blending of a counting mixture.
Ionisation Chamber (Flow)	"	"	Not capable of resolving activity due to C^{14} and H^3.
Solid Scintillator (Plastic)	60	10	No operational or economic advantage over above systems.
Liquid Scintillator	75	20	Must be used either as an integral or discontinuous detector, i.e. radioactivity of components is recorded additively or separate assays must be made of a solution of each component.

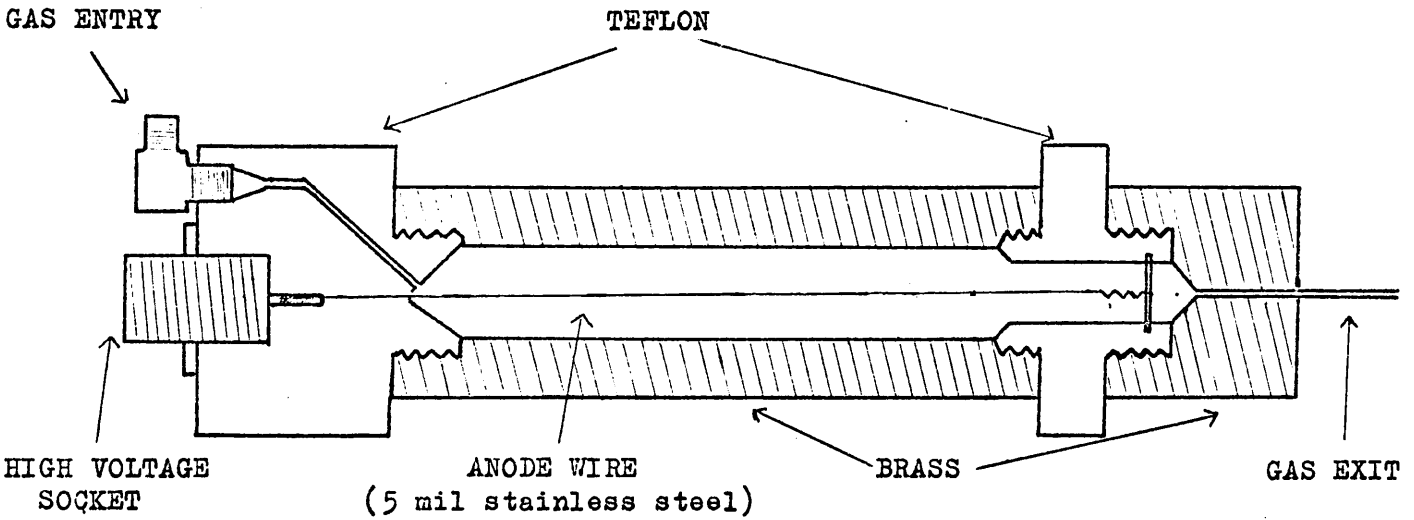


Figure 6. The Proportional Counter.

details of the counter are shown in figure 6.

The counter operated with a helium/methane (10:1) filling and the proportion of methane in this was accurately controlled by a needle valve which was located on the methane supply line ($\frac{1}{8}$"o.d. copper) before the junction with the chromatograph exhaust. After passing through the counter the helium/methane mixture could be diverted into a bubble flowmeter where the total flow rate was determined.

The arrangement of the instrumentation associated with the counter, high voltage supply, pulse amplification and counting, is shown in the general block diagram (figure 1). The power supply was by a Dynatron (type N103) unit, the output from which was continuously variable from 300 to 3,300 volts. The amplification was through a Dynatron (type 50D) pulse amplifier. This consisted of a high gain preamplifier, which was connected to the counter by as short a lead as was convenient (approx. 1 ft.) to minimise interference pick-up, and a main amplifier in which the gain could be altered in 2db. steps in the range 0-40db. This facility, operated in conjunction with the discriminator bias on the ratemeter and scaler used, permitted selection of the optimum conditions to detect pulses of a particular energy. Two

ratemeters were used at different times in the course of the work, an IDL 1815 series II and an Ekco N522C: the substitution of one by the other was to make use of the Ecko's variable discriminator to reduce the recorded background and match the ratemeter output to that of a high speed scaler (Ekco type 530D), with a dead time of 5 usecs, which was connected to the second output of the amplifier. Both ratemeters had 100mV recorder outputs which were connected to a "Servoscribe" potentiometric recorder where the activity in the eluted components was displayed as peaks. From the area of the peaks the total number of counts recorded could be measured. In practice it was more usual to use the recorder trace to determine when to start and stop counting with the scaler.

3.7 Calibration Procedure for the Proportional Counter.

The performance of the counter, like that of the chromatograph, was dependent upon day to day experimental conditions. Consequently the calibration procedure was again a dual process comprising of both an extensive pre-experimental investigation and also a brief check on both counter efficiency and reactant gas activity during each experiment. Although conditions in similar experiments were kept as uniform as possible it was not practicable to reproduce the exact sensitivities in

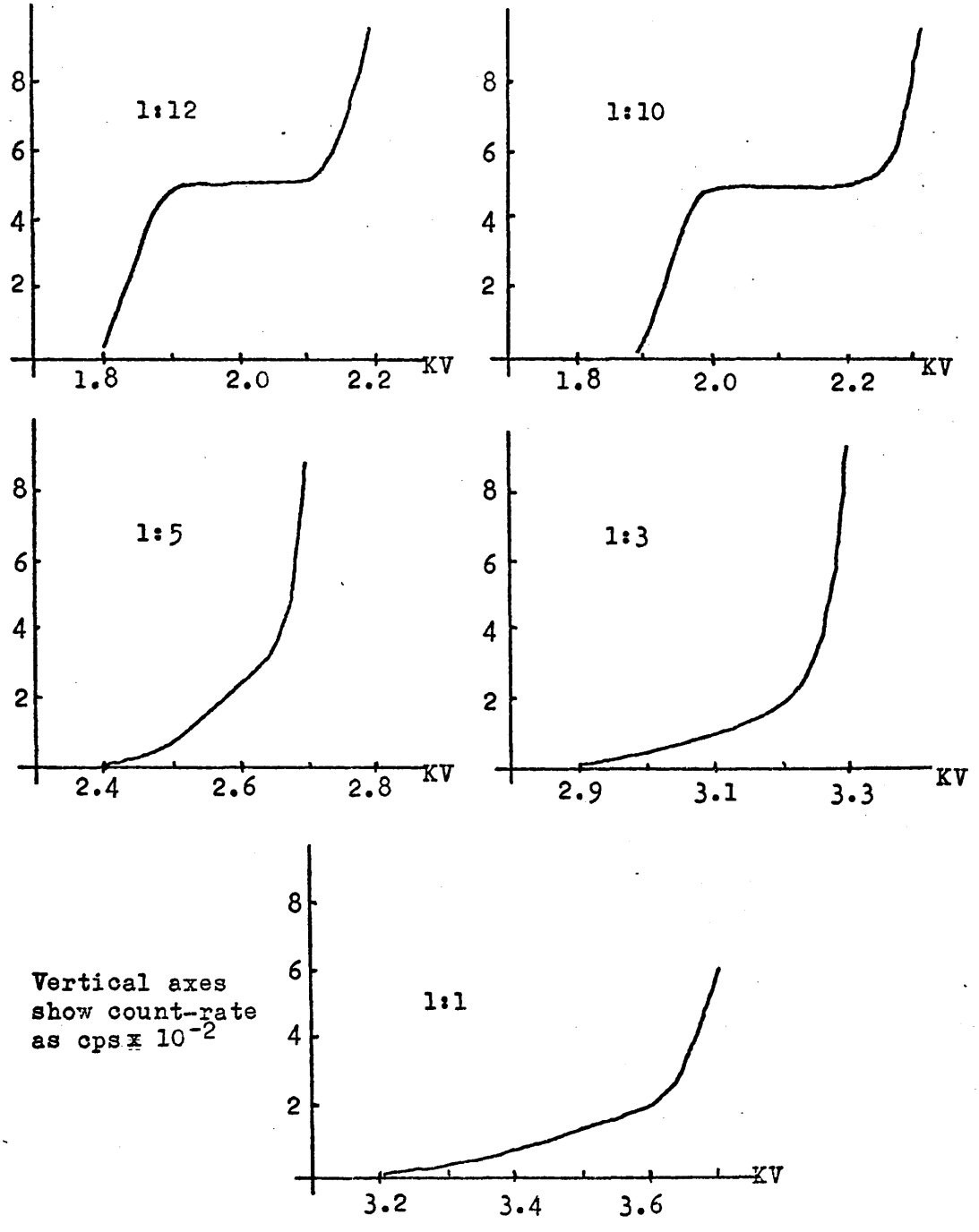


Figure 7. Dependence of Counter Plateau on Methane:Helium Ratio.

both the chromatograph and counter on every occasion.

(a) Plateau dependence on helium/methane ratio. A helium flow rate of 60 ml. min^{-1} had to be maintained for chromatographic separations and in a study of the helium/methane ratio, mixture proportions were altered by varying the methane flow rate. When the IDL rate-meter, with a fixed input threshold of 0.5 volt, was being used background noise had to be controlled from the amplifier. This was set to:

Attenuation	40 db.
Time Constant (Differentiation)	3.2 usec.
" " (Integration)	1.6 usec.

With these settings and using a Cs^{137} external source the variation of count rate against applied voltage was investigated for different helium/methane proportions (figure 7).

The optimum mixture for both plateau length and slope was found to be 10:1 helium/methane, which regularly gave a plateau of length greater than 200 volts and slope less than 3% per 100 volts. In order to determine the length of a plateau it was necessary to go instaneously beyond it into discharge. Re-determination of the plateau showed that it was shorter and steeper (figure 8 plateaux A & B). The stability of the mixture proportions was demonstrated by setting

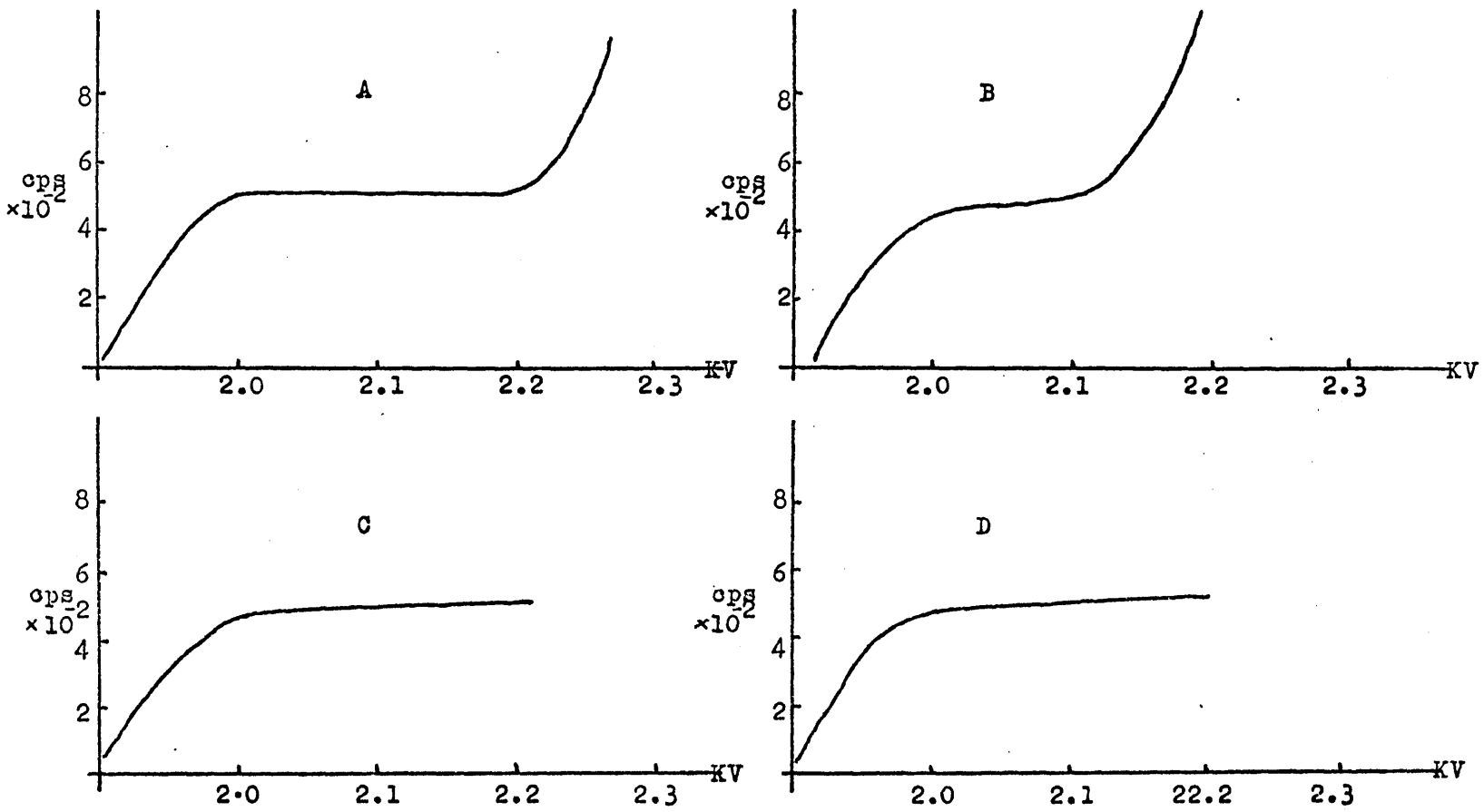


Figure 8. The "Discharge Effect" on the Counter Plateau.

the voltage in the plateau near the top end and running it for three hours. In another test successive plateaux with the same mixture were determined without going up to discharge voltages. This showed the plateau to retain its initial length and slope (figure 8 plateaux C & D).

(b) Background and Shielding.

The counter cathode, with brass walls almost ½" thick, acts as substantial shielding in itself c.f. a glass counter. Surrounding the counter completely with 8" x 4" x 1" lead bricks only reduced the background from 1.9 c.p.s. to 1.45 c.p.s. A partial shield, with a lead brick on either side and one on top which gave the same reduction in background was found more convenient in use.

(c) Proportionality.

Due to the low threshold of the IDL ratemeter and the consequent high attenuation, low gain setting of the amplifier, it was not possible to test the proportionality of the counter before the early experiments. This, however, was done when the Ecko N522C ratemeter was incorporated. The procedure[80] adopted was as follows: with a 1:10 methane to helium mixture, the amplifier gain set at 20 db. and the discriminators on the ratemeter and scaler at 5 volts, the applied

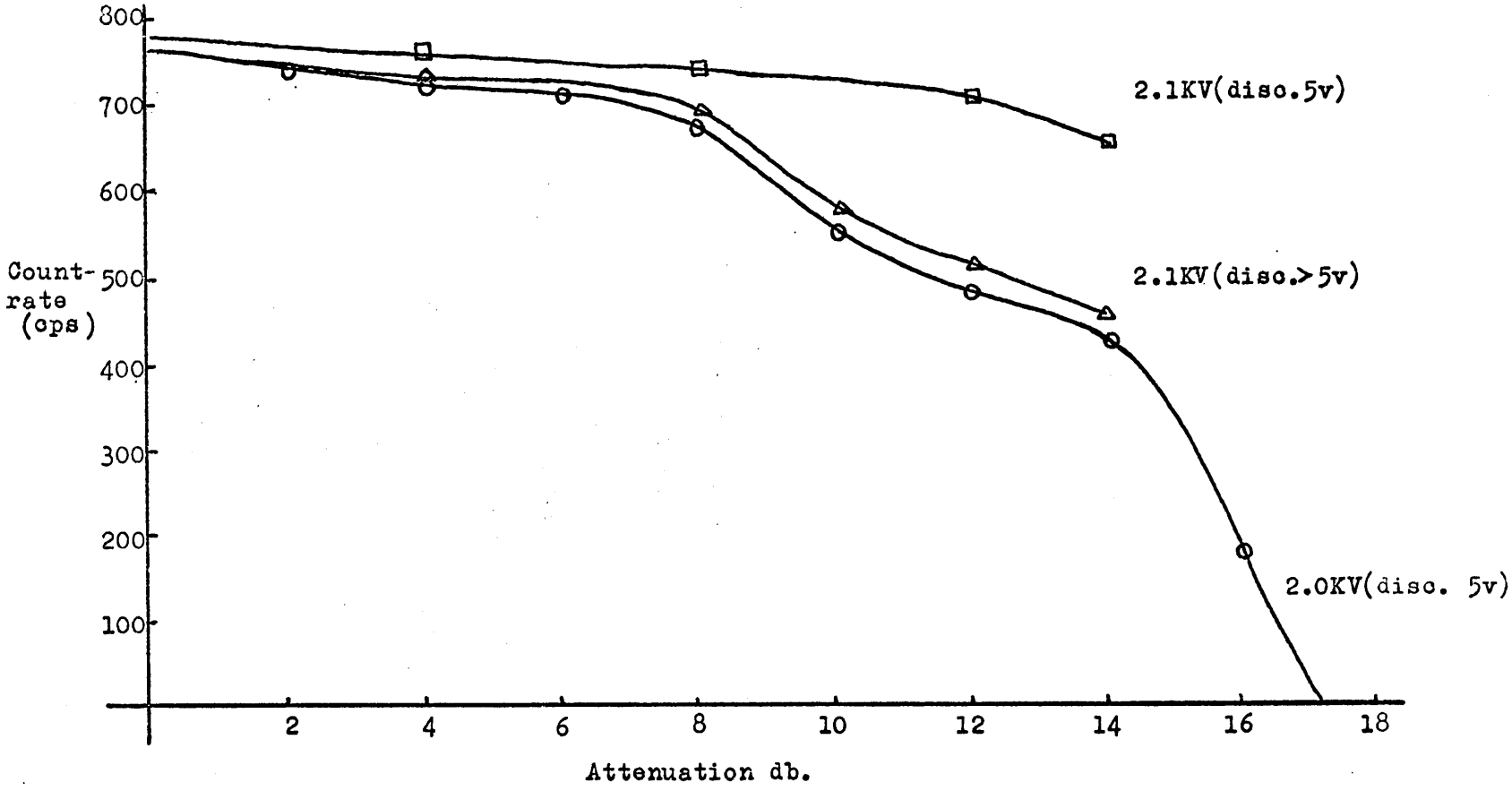


Figure 9. Test of Counter for Proportionality.

voltage was increased. No counting was observed at 2.0KV, a frequent plateau centre, but by reducing the attenuation to 16db. sporadic counting was noted and curve A (figure 9) was obtained by further stepping down. The applied voltage was increased by 100 volts and a second attenuation curve (B) was obtained. At 14db. on this curve, the discriminators were raised until the count fell to that recorded at 14db. on curve A i.e. at 2.0KV. Redetermination gave a graph very similar to, though not superposable on, curve A. This proved that the counter was operating in the proportional region i.e. that pulse heights were proportional to the initial ionising event.

(d) Quantitative Behaviour of the Counter.

The test of proportionality, interesting as it was, was much less critical for the problem than the tests described below in which the response of the counter to different quantities of injected radioactive gases was determined.

Before beginning the injection of labelled compounds, it was necessary to investiage the effect on the efficiency of the counter, of the passage through it, of the quantities of gases to be expected in the course of an experiment. This was easily accomplished for C-14 detection by placing a small piece of C-14

labelled methyl methacrylate polymer (Radiochemical Centre β -standard CFP3) in the counter, setting the voltage to the centre of a predetermined plateau and injecting up to 0.5 ml. of hydrogen, air, and ethylene. No fall from the plateau count rate which corresponded precisely with that expected from the standardised polymer sheet, was observed during the passage of any component. A conveniently sized tritium standard for incorporation in the counter was not available. Thus tests for the weaker β emission (0.018 MeV) were carried out by placing a Cs-137 source near the counter and altering the amplifier attenuation so that the pulses detected were of similar energies to those detected when tritium gas passed through the counter. Using this simulated tritium standard, 0.5 ml. of hydrogen and ethylene injected into the system again produced no significant change in count rate. In this test however the precaution was taken of setting the applied voltage at the upper end of the plateau. Thus any hydrocarbon effect would only be to shift the plateau temporarily so that the voltage setting moved relatively closer to the centre of the new plateau. The selection of ethylene as the test hydrocarbon in this investigation was on the grounds of its proposed use in the catalytic studies and because it has been shown, in larger doses,

to have a greater effect on counter performance than the saturated hydrocarbons.[81]

The conclusion from these tests was that any failure in the quantitative response from the counter would not be a result of the change in counter characteristics during the passage of a sample of 0.5 ml. or less.

Tritium was available as a gas in a "break seal" ampoule from The Radiochemical Centre, Amersham. A one curie sample, 0.4cc. at S.T.P. and of 98% isotopic abundance, was obtained and introduced to the apparatus as follows. The ampoule was glassblown on to the connecting vacuum line from a storage bulb on the apparatus and the whole section thoroughly degassed until a "holding" vacuum of better than 1×10^{-5} torr was obtained. Hydrogen, purified as detailed earlier, was admitted to a pressure of a few centimetres of mercury and the section again thoroughly evacuated. The pumps were then cut off, the break seal broken and hydrogen admitted until the pressure in the two litre reservoir was $\sim$700 torr. Dilution of this gas by a factor of 50, by transferring 0.1 litre. atmosphere to a five litre bulb and making up the pressure to approximately atmospheric, gave a sample of specific activity, 0.1 mc./ml. 2.0 ml. of this gave a twinned peak on

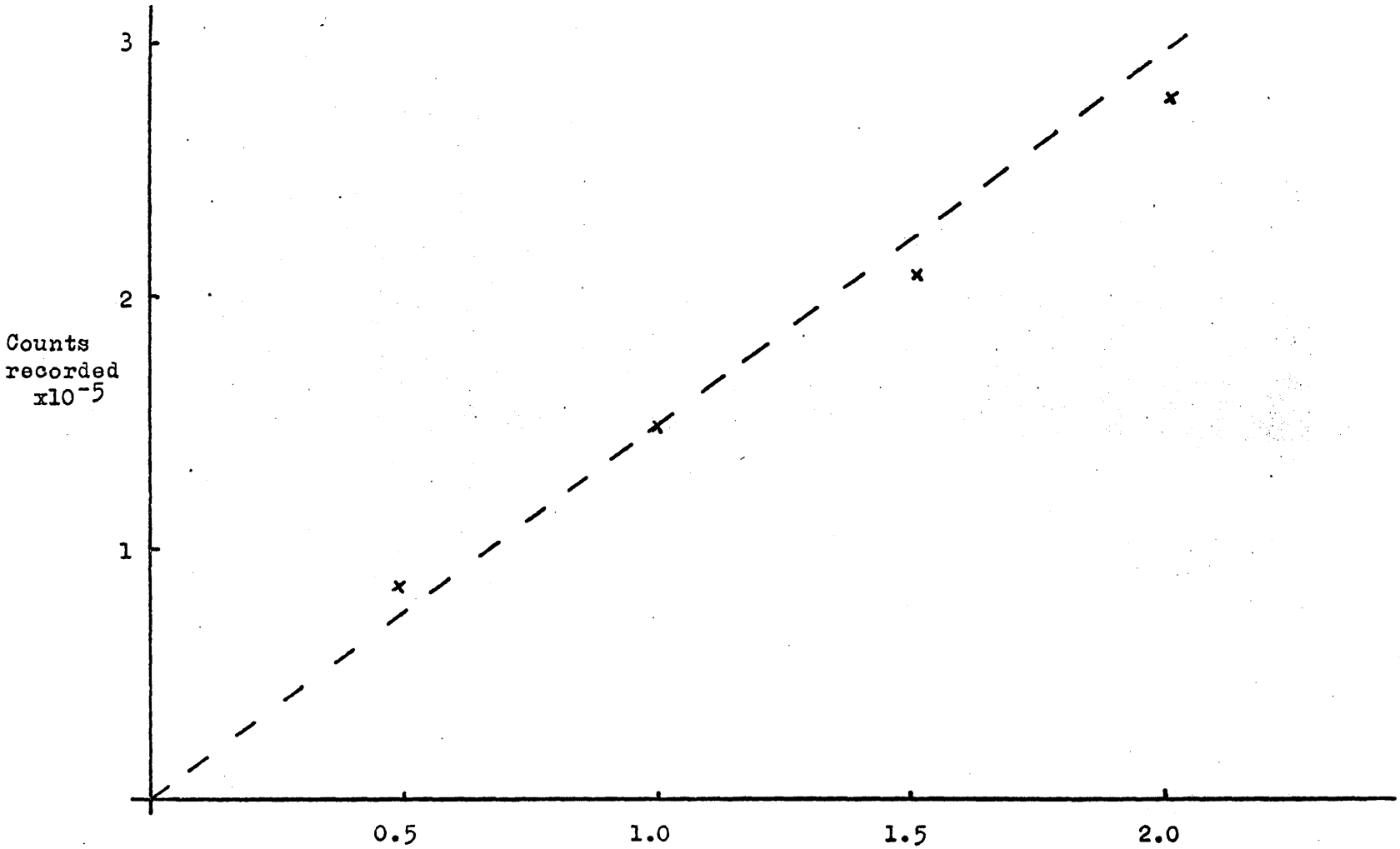


Figure 10. Specific Activity of Tritium.

the radiochromatograph, although the gas chromatograph indicated no contamination. Twinning of the hydrogen peak, a frequent occurrence in chromatography due to the similarity in thermal conductivity of hydrogen and helium, was attributed in this instance to a change in the characteristics of the counter. The efficiency might be lowered at the top of the peak and there would also be coincidence losses due to the high count rate at the peak maximum ($\sim$ 6 K c.p.s.). The expected use for tritium, in studies of exchange with hydrogen adsorbed on the catalyst after reduction, required a high specific activity rather than an exact quantitative relationship in the 2ml. range. Nevertheless the contents of the five litre bulb were diluted further (approx. tentimes) and the linear calibration shown in figure 10 was then obtained; the column temperature was 20°C.

Since it was impossible to repurify the hydrogen in the apparatus, the tritium was pumped out of the sample vessels after each series of injections had been withdrawn and this necessitated redilution of tritium from time to time by the extraction of aliquots from the two litre (approx. 0.9 curie) storage vessel. Although activities were always kept approximately the same, no attempt was made to reproduce the dilution

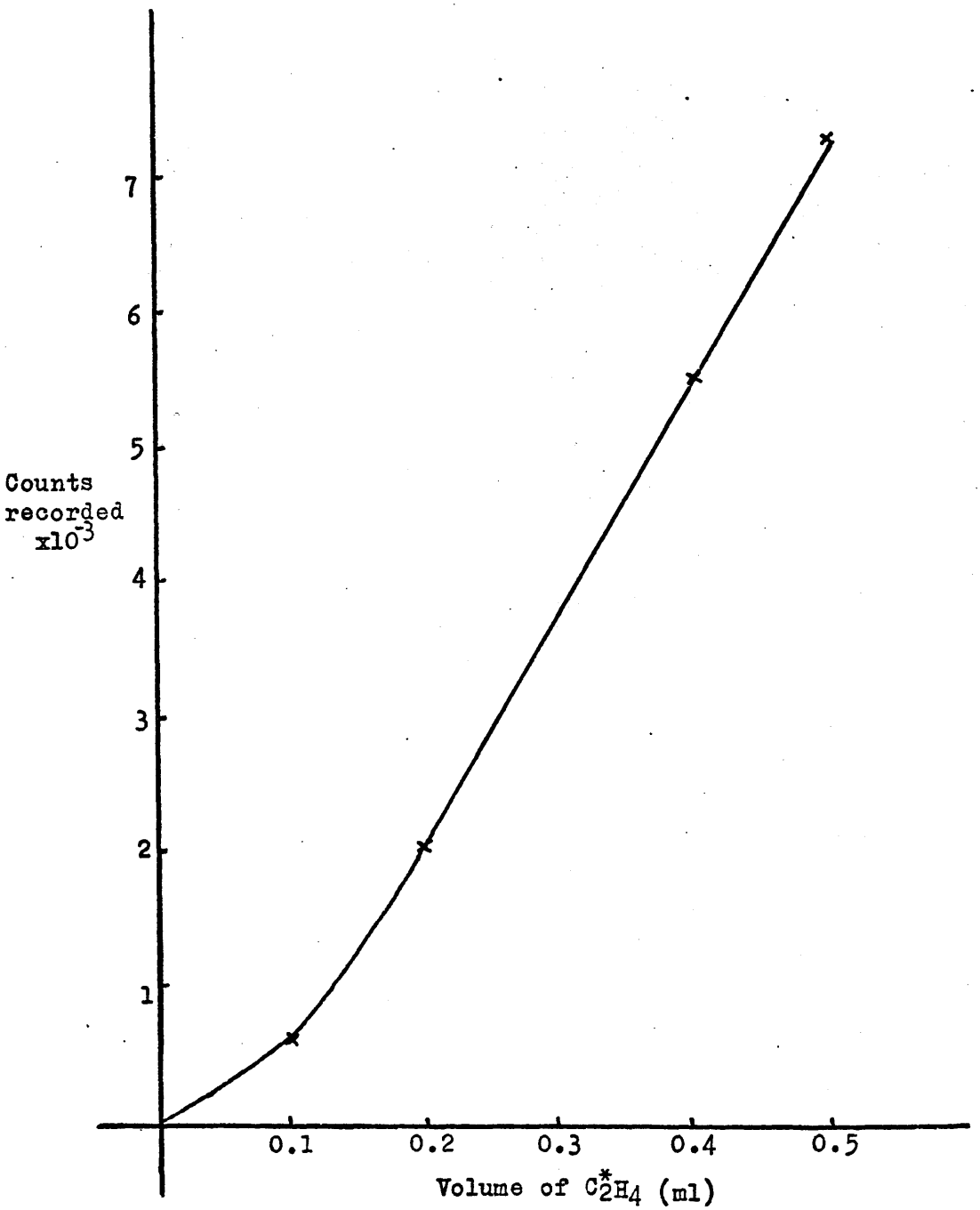


Figure 11. Specific Activity of C-14 Ethylene(I).

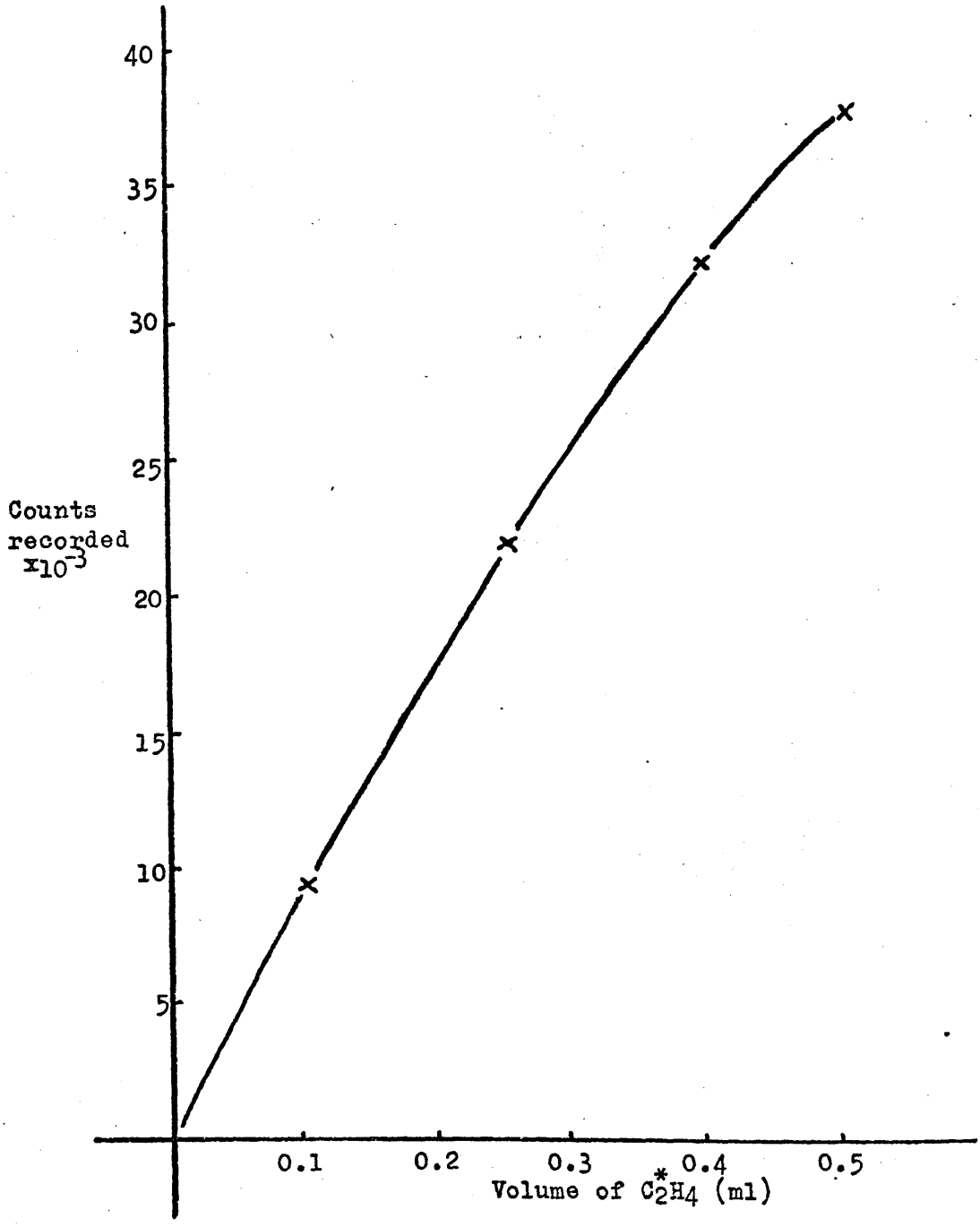


Figure 12. Specific Activity of C-14 Ethylene(II).

exactly as long as peak twinning or flattening was not observed at the column temperature to be used. The effect of raising the column temperature was to "sharpen up" the peak and make twinning more likely.

The radioactive ethylene to be used was supplied in ampoules by the Radiochemical Centre. 0.5 mc. of ethylene (specific activity 47.9 mc./mM.) was admitted to a storage vessel in the same way as the tritium and diluted by the transfer of purified ethylene stored in another bulb. Two batches were made up differing by a factor of five in their activity and both gave satisfactory quantitative calibrations (figures 11 and 12), the activities being such that coincidence losses were not expected with the quantities to be used in the catalytic experiments. C-14 ethane and acetylene were both detected by the counter in the diluted ethylene when a sample was analysed by the chromatograph, but the proportions, less than 0.001%, were of no chemical or catalytic significance. Attempts to reduce the impurities by fractionation were only partially successful and in practice activity corrections had always to be made when small quantities of ethane were recovered from an injection. It was assumed, on the basis of a preliminary experiment, that ethane was not adsorbed by the catalysts (Section 4.2.iii) and the

ethane activity in the calibration injection was subtracted from that observed in any subsequent reaction analysis.

3.8 Experimental Procedure.

The experiments performed can be classified into four types each differing in its object and in the way in which it was executed.

(a) Studies of Hydrocarbon Retention by the Palladium Catalyst.

This series of experiments was designed to find a convenient gas volume to catalyst ratio in order that the amount of a particular gas adsorbed by the catalyst could be measured. Then, when conditions had been established which led to reproducibility, the intention was to investigate the variation in the amount of various hydrocarbons adsorbed by the catalyst at a series of temperatures, 20°C, 100°C and 200°C. These temperatures were chosen to give a wide range in which a change in the mode of adsorption of a hydrocarbon might occur. The procedure established for these experiments, which were conducted throughout with the palladium catalyst, was as follows:

(i) The serum caps on the gas handling vacuum apparatus were renewed and the sample vessels, manometers, and connecting manifolds were evacuated.

(ii) A small silica wool plug was inserted into the bulb of the catalyst vessel and 0.50 g. of catalyst was placed on top of this and compacted by tapping the vessel.

(iii) New serum caps were put into the injection ports, the thermocouple inserted into the well provided on the vessel, the furnace slipped over the vessel, tubing connections remade and the whole section reassembled on to the switch valves SV1 and SV2.

(iv) The switch valves were so arranged that the catalyst by-pass circuit was complete and the helium flow rate was increased from the overnight flow rate of 2 to 5ml.min^{-1} to the working 60ml.min^{-1}. The column temperature was increased to the working temperature, 70 or 130^{o}C in the case of most silica gel column experiments.

(v) The hydrogen line was connected to the catalyst side of the switch valves and the fine control valve on it opened slowly until a flow rate of approximately 30ml.min^{-1}. was passing over the catalyst and through a gas bubbler connected to the exhaust from SV2. After hydrogen had been allowed to flow for five minutes to remove air from the system, the temperature of the catalyst was raised to 200^{o}C. At this temperature the reduction/

/activation was carried out for 30 minutes. This meant that the catalyst was in a hydrogen atmosphere for approximately one hour.

(vi) Towards the end of the reduction period, with the helium flowing round the by-pass, the chromatograph filament current was turned up to the working 200mA and the zero adjustment was set to give a steady and conveniently placed base line. The filament current was then returned to zero.

(vii) After the reduction period the hydrogen cylinder valve was closed and as the flow rate fell, as seen on the exit bubbler, the helium flow was switched over the catalyst. To remove the bulk of the gas phase hydrogen in the system the helium and hydrogen were allowed to exit through the bubbler and the laboratory exhaust for a few seconds. SV2 was then turned to divert the flow into the chromatograph. The filament current was turned up to 200mA, the recorder switched on, and the return of the pen to the base line, as the hydrogen concentration in the helium fell, was observed.

(viii) During the "helium cleaning" period the sample gas to be investigated was pressurised to approximately 1.25 atmospheres. This was done by transferring some gas from the appropriate reservoir

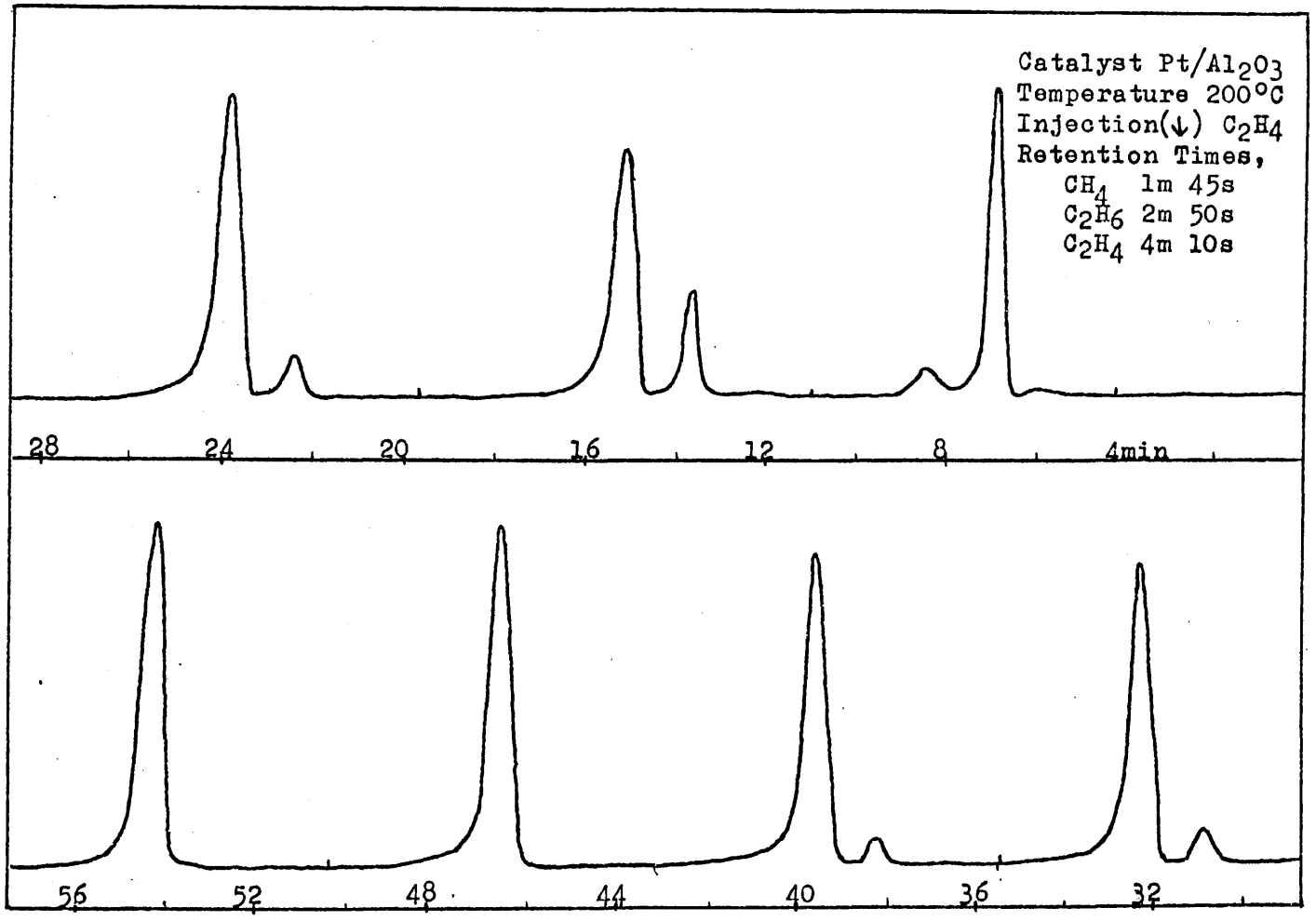


Figure 13. Chromatograph Trace from Typical Experiment.

to a sample vessel, condensing it and repeating the cycle until, on re-evaporation, the vessel contained the required super-atmospheric pressure as measured on an open ended manometer.

(ix) Tests for reproducibility indicated that injections could be commenced after flowing helium over the catalyst for as little as 30 minutes, the results of an injection at this time being no different from those obtained after flowing the helium for four hours. After this 30 minute period the catalyst temperature was adjusted to that required for the investigation. The hydrocarbon injection sequence was usually as follows: two 0.5ml. samples of the hydrocarbon were injected in IP2, the calibration port: successive similar injections (from two onwards) were made over the catalyst (IP1): and if the experiment was particularly long a check calibration 0.5ml. (IP2) was introduced at the conclusion of the experiment. A typical reaction trace, in which the calibration was carried out after reaction injections, is shown in figure 13.

(b) Studies of Hydrogen Retention by the Catalysts (I).

The second series of experiments involved the use of tritium in a post-reduction treatment of the

catalysts. These were designed to investigate the efficiency of the helium treatment for the removal of hydrogen from three different catalysts, palladium, rhodium, and platinum.

10ml. of tritium, pressurised by contraction rather than condensation at -195°C, was injected into the slowing hydrogen stream (a.vii) and the catalyst section was then isolated. The tritium was allowed to stand in contact with the catalyst for one hour. During this time, as well as testing the chromatograph zero setting, the counter plateau was determined and the background count rate measured. Switching the helium stream over the catalyst was then carried out as before (a.vii) to remove the hydrogen/tritium adsorbed on the catalyst but no quantitative measurement of the tritium adsorbed or desorbed was attempted. The helium was allowed to flow until the count rate from tritium showed no measurable fall and the injections of hydrocarbon were made as in procedure (a).

(c) Studies Involving C-14 Ethylene Adsorption on the Catalysts.

The "C-14 ethylene adsorption" experiments were designed to investigate the properties of the adsorbed portion of the gas injected for one sample gas, ethylene. The procedure in these experiments

was essentially similar to that described in the previous section (b). Although no tritium was introduced, the helium was allowed to flow for as long as the relevant (b) experiment showed it to be necessary. The determination of the counter plateau and the background count rate was made while the helium was passing over the catalyst immediately prior to commencing the hydrocarbon injections. After calibration, injections were made of up to three samples using C-14 ethylene. Successive samples were of inactive ethylene, acetylene or hydrogen, depending on the aim of the particular experiment.

(d) Studies of Hydrogen Retention by the Catalysts (II).

The final series of experiments was undertaken after it was shown that the high background count rate observed during the first tritium series (b) was not only a function of the low discriminator setting but also was due to the initial irreversible adsorption of a quantity of tritium on to the inside walls of the counter. This was removed by heating the counter to 150°C and maintaining this temperature overnight with helium flowing through the counter. The background count rate of 6c.p.m. did not rise during this series. In these experiments it was hoped to in-

-vestigate the amount of tritium exchanged and retained by each of the three catalysts and to measure the time of flow of helium over the catalysts after which no tritium was observed in the helium stream. The adsorption of ethylene and the incorporation of tritium in the products eluted was also to be measured.

The procedure was as described in section (b) except that 2ml. of tritium was injected into the helium stream as soon after this was switched over the catalyst, as counter calibration would permit. No attempt to allow the tritium to come into equilibrium with the hydrogen adsorbed during the reduction/activation period was made.

CHAPTER FOUR

THE RESULTS

4.1 Introduction.

Three series of experiments were conducted. The first series was an investigation of the variation, with temperature and type of hydrocarbon, of the retention of successive hydrocarbon doses by the palladium catalyst. This did not involve the use of any labelled reactants.

The second series was planned on the basis of the observation in the first series of high alkane yields from the injection of alkenes. It was designed to test the efficiency of flowing helium as a post-reduction treatment for the removal of hydrogen from the surface of the catalyst. This was done for the three catalysts (Pd, Rh, Pt) by treating them with tritium after the initial reduction/activation period, monitoring the effluent with the proportional counter and measuring the tritium incorporation in the products of ethylene and acetylene injections. Both static and flow treatments by tritium were used, the latter in an attempt to measure the amounts adsorbed by the catalysts.

The last series of experiments was designed to investigate some of the properties of, and hence

obtain information about, the nature of the adsorbed species retained by the catalysts when exposed to ethylene. The initial injection was of C-14 ethylene and subsequent injections, in different experiments, were of inactive ethylene, acetylene, and hydrogen. This series covered all three catalysts, each at three temperatures.

4.2. Studies of Hydrocarbon Retention by the Palladium Catalyst.

4.2.i. Presentation of Results.

In the first series of experiments but-1-ene and ethylene were used to determine the conditions which would give rise to measurable retentions. The principal variables were catalyst charge and quantity of hydrocarbon. A ratio of 0.5ml hydrocarbon to 0.50g of catalyst was established.

In several experiments at the same temperature, fluctuations in the retention of ethylene were observed. These were attributed to variations in the time of reduction and helium treatment. Since the influence of temperature was of primary interest in this study it was thought necessary to adopt standard conditions of pretreatment. These consisted of 30 min. to one hour in flowing hydrogen at 200°C, followed by a similar time in flowing helium at 200°C, before

cooling, if necessary, to the reaction temperature. The reduction time was chosen with reference to the known ease of reduction of palladium catalysts and the helium - treatment time was twice the time taken for the chromatograph to show a steady base line i.e. a carrier gas of constant composition. In subsequent experiments the helium flowed for longer periods (up to 8 hours). This increase did not significantly alter the retentions or the composition of the eluant.

Two experiments, one with ethylene the other with but-1-ene, were carried out to test the hydrogenation activity of the catalyst after the above pretreatment. 2.4ml of an approximately 1:1:: hydrocarbon:hydrogen mixture was injected over 0.24g of the palladium catalyst which had been activated by the standard procedure. Total conversion to the saturated hydrocarbon was obtained in both experiments for as many doses as were made. The butene experiment was conducted at 100°C, the ethylene one at 20°C.

Results of the adsorption studies of the various hydrocarbons are given in the following sections and the presentation includes the complete analysis of at least one experiment for each gas and retention and eluant analysis of every initial dose.

4.2.ii. Ethylene Adsorption on the Palladium Catalyst.

Typical Multiple-Dose Experiments.

The catalyst (0.50g) was reduced for one hour at 200°C and thereafter treated with helium for one hour before the dosing with ethylene (0.5ml) was commenced. In the second and third experiments, at 100°C and 20°C respectively, the catalyst was reactivated as above, and maintained at 200°C for 30 min in the helium flow before cooling in helium to the reaction temperature.

TABLE 7.

Complete Analysis of Ethylene Adsorption Experiments on Pd/Al_2O_3

Experiment & Injection Number	Eluant Analysis Ethane ml	Eluant Analysis Ethylene ml	Hydrocarbon recovered as % carbon injected.	Hydrogenated eluant as % hydrocarbon recovered.
I.1.(200°C)	0.30	-	61	100
2.	0.29	0.02	62	93
3.	0.18	0.22	80	45
4.	0.09	0.38	94	19
5.	0.06	0.43	98	12
6.	0.05	0.44	98	10
II.1.(100°C)	0.33	-	66	100
2.	0.23	0.145	75	61
3.	0.04	0.41	90	9
III.1.(20°C)	0.27	0.03	60	90
2.	0.12	0.28	80	30

0.01 ml methane was recovered from injection I.1 at 200°C.

Comparison of the Analyses of First Doses of Ethylene.

In all the experiments a series of 0.5ml injections of ethylene were made into the helium stream above 0.50g of the catalyst which had been reduced/reactivated at 200°C. Table 8 shows only the analysis for the first injection.

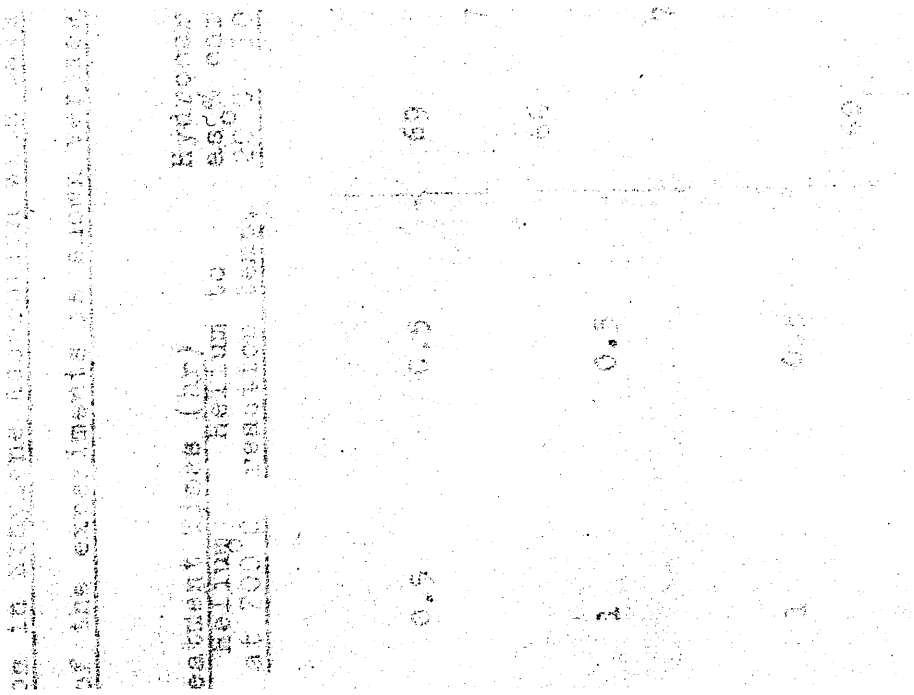


TABLE 8.

Variation in Ethylene Adsorption with Catalyst Temperature.

The order of the experiments is shown vertically. Catalyst, Palladium.

Pretreatment Times (hr) Hydrogen Reduction	Helium at 200°C	Helium to reaction temp.	Hydrocarbon recovered as % carbon injected. 20°C	100°C	200°C	Hydrogenated eluant as % hydrocarbon recovered.
					58	100 (5,CH_4)
0.5	0.5	0.5	69		-	100
				75		100
			66			97
2	1	0.5			59	100 (5,CH_4)
				76		100
				66		100
1	1	0.5			58	100 (10,CH_4)
			60			90

Each of these experiments was carried out on the same sample of catalyst and the experiments were performed in the order shown. This was designed to test the efficiency of the reduction treatment for the removal of residues and to establish that the order of temperature variation was not the significant factor in determining the retention.

The average total hydrocarbon recovered from all the experiments with ethylene, regardless of pretreatment is shown in table 9 together with the number of experiments at each temperature.

TABLE 9.

Average Values of Hydrocarbon Recovered From First Injections

Injection, 0.5ml Ethylene	Catalyst, Pd/Al_2O_3		
Catalyst Temperature	20^oC	100^oC	200^oC
Hydrocarbon Recovered (as % carbon injected)	67	69.5	60
Number of Experiments	9	8	10

4.2.iii Ethane and Methane Adsorption on the Palladium Catalyst.

The presence of ethane and methane in the eluant from ethylene injections necessitated an investigation of the adsorption of these hydrocarbons, before conclusions could be drawn from the retention results.

The pretreatment conditions were uniform throughout: one hour in flowing hydrogen at 200°C, 30 min in flowing helium at 200°C and 30 min in flowing helium as the catalyst was cooled to the reaction temperature.

TABLE 10.

Complete Analysis of Ethane Adsorption Experiments on Pd/Al_2O_3.

Experiment & Injection No.	Eluant Analysis Methane ml	Eluant Analysis Ethane ml	Hydrocarbon recovered as % carbon injected.
I.1.(200°C)	0.01	0.465	94
2.	0.005	0.475	95.5
II.1.(100°C)	-	0.47	94
2.	-	0.485	97
III.1. (20°C)	-	0.44	88
2.	-	0.465	93

TABLE 11.

Complete Analysis of Methane Adsorption Experiments

Pd/Al_2O_3

Experiment & Injection No.	Eluant Analysis Methane ml	Hydrocarbon recovered as % carbon injected.
I.1.(200°C)	0.48	96
2.	0.49	98
II.1.(100°C)	0.48	96
III.1.(25°C)	0.49	98
	0.49	98

4.2.iv Acetylene Adsorption on the Palladium Catalyst.

Consideration of the surface species responsible for the unrecovered portion of the ethylene injections e.g. whether ethylenic, acetylenic, or polymeric etc. made a study of acetylene adsorption desirable. This was carried out under the standard conditions of one hour in hydrogen and a total of one hour in helium unless otherwise stated. Because of the range of products eluted the results are shown as the full analysis of the first dose in each experiment (table 12).

TABLE 12.

Variation in Acetylene Adsorption with Catalyst Temperature.

Catalyst, Palladium.

Temperature of Catalyst.	Analysis of First Dose				Hydrocarbon recovered as % carbon injected.
	Methane ml	Ethane ml	Ethylene ml	Acetylene ml	
200°C	0.03	0.06	-	-	15
"	0.015	0.09	-	-	19
"	0.02	0.09	0.005	-	21
"	0.01	0.08	0.005	-	18
"	0.01	0.08	0.005	-	18
100°C	-	0.04	-	0.01	10
"	-	0.05	-	0.01	12
20°C	-	0.005	-	0.06	13
"	-	-	-	0.085	17
"	-	0.05	-	0.045	19
"	-	0.05	-	0.04	18
"	-	0.01	-	0.06	14

In the last three experiments the usual 30 min period in helium at 200°C was omitted and the catalyst was cooled in helium immediately after reactivation.

4.2.v Propylene Adsorption on the Palladium Catalyst.

To study the effect on retention of hydrocarbon chain length a series of experiments with propylene was undertaken. The analysis of a complete experiment (three injections at 200°C) is shown in table 13, first dose analysis for the remaining experiments in table 14, and hydrocarbon recovery as a function of temperature in table 15.

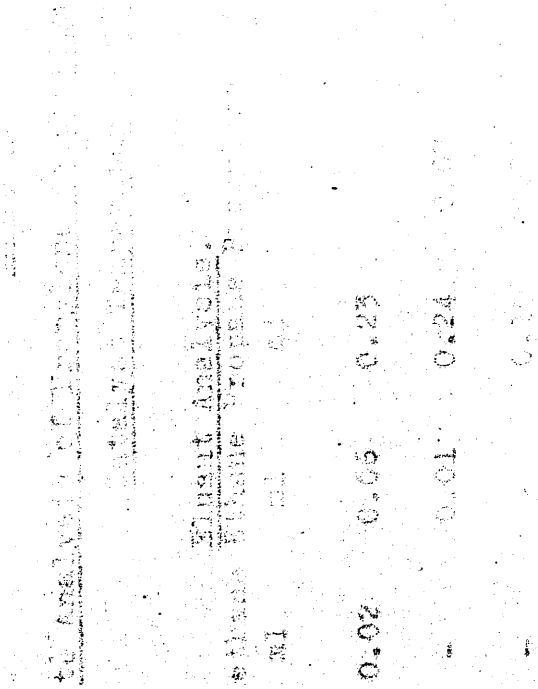


TABLE 13.

Complete Analysis of Propylene Adsorption Experiment on Pd/Al_2O_3

Catalyst Temperature 200°C.

Injection Number	Eluant Analysis. Methane ml	Ethane ml	Propane ml	Propylene ml	Hydrocarbon recovered as % carbon injected.	Hydrogenated eluant as % hydrocarbon recovered.
1	0.02	0.06	0.23	-	56	100
2	-	0.01	0.24	0.07	64	78
3	-	-	0.10	0.27	74	27

TABLE 14.

Variation in Propylene Adsorption with Catalyst Temperature

Catalyst, Palladium

Experiment No. & Temperature of Catalyst (°C)	Eluant Analysis Ethane ml	Propane ml	Propylene ml	Hydrocarbon recovered as % carbon injected.	Hydrogenated eluant as % hydrocarbon recovered.
1.200	0.05	0.23	-	54	100
2.100	-	0.24	0.06	60	80
3. 20	-	0.31	0.07	76	81
4.200	0.02	0.31	-	65	100
5.200	0.015	0.30	0.04	70	88
6.100	-	0.22	0.17	78	56
7.100	-	0.17	0.19	72	48
8. 20	-	0.22	0.17	78	56
9. 20	-	0.21	0.14	70	60
10.200	0.015	0.29	0.02	64	94
11.100	-	0.22	0.15	74	60
12. 20	-	0.14	0.21	70	40
13.200	0.015	0.29	0.02	64	94
14.100	-	0.28	0.05	66	85
15.200	0.04	0.24	0.03	58	89
16.200	0.04	0.27	0.03	64	91
17.100	-	0.26	0.10	72	72
18.100	-	0.23	0.10	66	70
19. 20	-	0.16	0.12	56	57
20.200	0.10	0.20	-	57	100
21.200	0.05	0.26	-	60	100
22.100	-	0.29	0.025	63	92
23.200	0.06	0.23	-	55	100
24.200	0.09	0.23	-	62	100

In addition to those shown above, yields of 0.02, 0.06 0.015, 0.02, and 0.04 ml of methane were obtained in experiments 1, 20, 21, 23, and 24 respectively.

The experiments were carried out in the order shown and catalyst was replaced after experiments 3, 14, 19 as shown

by the separating line. In the last series, experiments 20-24, injections were made 30 min after activation and in the experiment at 100°C (No.22) the catalyst was cooled to 100°C without any helium treatment at 200°C. These experiments and the immediately preceding one at 20°C (No. 18) have been omitted from the averages in table 15.

TABLE 15.

Average Values of Hydrocarbon Recovered from First Injections.

Injection, 0.5ml Propylene	Catalyst, Pd/Al_2O_3		
Catalyst Temperature	20°C	100°C	200°C
Hydrocarbon Recovered (as % carbon injected)	74	70	67
Hydrogenated Eluant (as % hydrocarbon recovered)	59	67	94
Number of Experiments	4	7	7

4.2.vi Propane Adsorption on the Palladium Catalyst.

As in 4.2.iii. an investigation of the adsorption of the corresponding alkane was considered necessary and a short series of experiments with propane was carried out. The results of a complete experiment at 200°C are shown in table 16, and first dose analysis of the remaining experiments in table 17.

TABLE 16.

Complete Analysis of Propane Adsorption Experiment on Pd/Al_2O_3

Catalyst Temperature 200°C. Injection 0.5ml propane.

Injection Number.	Analysis of Eluant			Hydrocarbon recovered as % carbon injected.
	Methane ml	Ethane ml	Propane ml	
1	0.01	0.04	0.40	86
2	0.005	0.03	0.45	94.5
3	-	0.02	0.455	94
4	-	0.01	0.47	95

TABLE 17.

Variation in Propane Adsorption with Catalyst Temperature

Catalyst, Palladium

Temperature of Catalyst (°C)	Analysis of Eluant			Hydrocarbon recovered as % carbon injected.
	Methane ml	Ethane ml	Propane ml	
100	-	-	0.50	100
200	0.02	0.04	0.40	86.5
20	-	-	0.50	100
200	0.02	0.055	0.41	90
200	0.005	0.04	0.43	91.5

4.2.vii Cyclopropane Adsorption on the Palladium Catalyst.

A study of the adsorption of cyclopropane was undertaken to discover whether cyclopropane gave retention values similar to the alkenes (26-37%) or the alkanes (0-14%). The analysis of two injections of an experiment at 200°C, in which helium flowed over the catalyst for four hours, is shown in table 18. First dose analyses of the other experiments, conducted with the standard pretreatment of one hour in hydrogen and helium, are shown in table 19.

TABLE 18.

Complete Analysis of a Cyclopropane Adsorption Experiment on Pd/Al_2O_3.

Catalyst Temperature 200°C.

Injection Number.	Eluant Analysis					Hydrocarbon recovered as % carbon injected.
	Methane ml	Ethane ml	Propane ml	Cyclopropane ml	Propylene ml	
1	0.005	0.025	0.255	0.03	0.01	61
2	-	-	0.21	0.11	0.08	80

TABLE 19.

Variation in Cyclopropane Adsorption with Catalyst Temperature.

Catalyst, Palladium

Temperature of Catalyst (°C)	Eluant Analysis					Hydrocarbon recovered as % carbon injected.
	Methane ml	Ethane ml	Propane ml	Cyclopropane ml	Propylene ml	
200	0.01	0.05	0.27	0.05	0.02	72
"	0.01	0.045	0.27	0.04	0.01	67.5
100	-	-	0.33	0.01	-	68
20	-	-	0.135	0.29	-	85
200	0.005	0.015	0.27	0.035	0.015	65.5
100	-	-	0.37	0.02	-	78
"	-	-	0.38	0.035	-	83

4.2.viii But-1-ene Adsorption on the Palladium Catalyst.

As indicated previously the adsorption of but-1-ene was never studied under the standard conditions established. The results shown in table 20 were obtained using:

(1) a helium flow rate of 40 ml min^{-1}

(2) a catalyst charge of 0.18g.

and (3) a but-1-ene injection of 2.4 ml.

The chromatographic analysis employed a 12ft. column of 30% Dimethyl Sulpholane on C-22 Firebrick, 42-60 mesh. This was operated at room temperature. Calibration using the planimeter indicated no significant loss of precision by assuming the same sensitivity for all the products and this was determined by but-1-ene calibration in each experiment. No adsorption was detected above room temperature where $\sim$18% of hydrocarbon was retained by the catalyst. The complete analysis of several injections in each experiment is shown in table 20.

TABLE 20

Complete Analysis of But-1-ene Adsorption Experiments on Pd/Al_2O_3.

Experiment and Injection No.	Analysis of Eluant				$\frac{(t\text{-but-2-ene})}{(c\text{-but-2-ene})}$
	Butane ml	But-1-ene ml	t-But-2-ene ml	c-But-2-ene ml	
I.1. (220°C)	0.32	0.24	1.10	0.65	1.70
2.	0.04	0.37	1.14	0.83	1.37
3.	0.03	0.70	1.00	0.80	1.25
II.1. (220°C)	0.08	0.24	1.16	0.65	1.78
2.	0.03	0.56	1.05	0.75	1.40
3.	-	0.95	0.79	0.65	1.22
III.1. (150°C)	0.075	0.465	1.07	0.70	1.53
2.	-	0.915	0.81	0.64	1.26
IV.1. (150°C)	-	0.45	1.14	0.75	1.52
2.	-	0.85	0.88	0.715	1.23
3.	-	1.09	0.70	0.62	1.13
V.1. (100°C)	-	0.85	0.84	0.61	1.38
2.	-	1.07	0.70	0.625	1.12
3.	-	1.55	0.41	0.42	0.98
VI.1. (20°C)	0.03	0.73	0.45	0.78	0.58
	-	1.86	0.35 (non-resolvable)		

4.2.ix Summary

The adsorption results are summarised in table 21.

TABLE 21.

Percentage of Initial Hydrocarbon Dose retained by the Palladium Catalyst.

	20°C	100°C	200°C
Methane	2	4	4
Ethane	12	6	6
Ethylene	33	31	40
Acetylene	84	89	82
Propane	0	0	10.5
Propylene	26	30	37
Cyclopropane	15	23.5	31.5

4.3 Studies of Hydrogen Retention by the Catalysts.

4.3.i Presentation of Results.

This series of experiments was designed to investigate the relative importance of (a) self-hydrogenation and (b) hydrogen retained by the catalyst following reduction, in the formation of alkanes from the injection of unsaturated hydrocarbons. The investigation was carried out using ethylene and acetylene and three alumina - supported catalysts, palladium, rhodium, and platinum. The variation in behaviour with temperature was not studied as exhaustively as in the first series, most measurements being made at 200°C.

As detailed in chapter 3, two procedures were adopted: (a) a static exchange in which 10ml of tritium was injected and left in contact with the catalyst for an hour before the helium flow was started; and (b) a flow treatment in which 2ml of tritium was injected into the helium stream and an attempt made to measure the amount retained by the catalyst.

The results presented in this section include the time of the helium treatment (60ml.min^{-1} at 200°C) after which no fall in the count-rate of the helium stream was detectable and the chemical

and radioactivity analysis of the subsequent hydrocarbon injections. In the static tritium exchange experiments the times of the helium treatment to reduce count-rates to background should be treated with caution, for there was, in this case, some adsorption of tritium on the walls of the counter (3.8.d.).

Some explanation is required for the unit to be used in describing the radioactivity of the eluted species. When a quantity of active material passed through the counter the total number of counts was recorded. The number of ml of this species was known from the chromatographic analysis and so a specific activity (which is not absolute) is computed in each case as total counts per ml. This is abbreviated in the tables to cpml x 10^{-5}.

4.3.ii Ethylene and Acetylene Adsorption on the Palladium Catalyst.

Five experiments were conducted on the palladium catalyst after a static exchange between tritium and hydrogen remaining on the surface after reduction. The results of the ethylene experiments are shown in table 22 and those of the acetylene experiments in table 23. In both tables the complete analyses of three injections for each experiment are shown.

TABLE 22.

Ethylene Adsorption after Static Tritium Exchange

Catalyst, Pd/Al_2O_3 Temperature, 200°C

Helium-treatment time 2 hours in experiment I

5 hours in experiments II & III

Experiment & Injection Number.	Eluant Analysis						Hydrocarbon recovered as % carbon injected.
	Methane		Ethane		Ethylene		
	ml	cpm1.10^{-5}	ml	cpm1.10^{-5}	ml	cpm1.10^{-5}	
I.1.	0.01	1.0	0.26	1.7	-	-	53
2.	-	-	0.22	1.5	0.05	0.4	54
3.	-	-	0.19	1.4	0.13	0.5	64
II.1.	0.01	1.6	0.27	2.1	-	-	55
2.	0.005	1.6	0.28	1.6	0.02	0.9	60
3.	-	-	0.18	1.4	0.16	0.8	68
III 1.	0.005	0.2	0.29	0.9	0.005	0.2	59
2.	-	-	0.25	0.6	0.12	0.2	74
3.	-	-	0.19	0.4	0.20	0.2	78

TABLE 23.

Acetylene Adsorption after Static Tritium Exchange

Catalyst, Pd/Al_2O_3 Temperature, 200^0C in experiment IV
100^0C in experiment V

Helium-treatment time, 6 hours in both experiments

Experiment & Injection Number.	Eluant Analysis						Hydrocarbon recovered as % carbon injected.
	Ethane		Ethylene		Acetylene		
	ml	cpm1.10^{-5}	ml	cpm1.10^{-5}	ml	cpm1.10^{-5}	
IV.1.	0.07	1.7	-	-	-	-	14
2.	0.08	1.3	0.01	*	0.005	1.2	19
3.	0.06	1.0	0.04	*	0.01	0.3	22
V.1.	-	-	0.02	0.9	0.09	-	22
2.	-	-	0.01	1.1	0.35	-	72
3.	-	-	0.01	0.7	0.35	-	72

* Resolution of the activity due to ethane and ethylene was not possible and the "specific" activity of both is shown under ethane. The incorporation of the high speed scaler permitted resolution in subsequent experiments.

4.3.iii Ethylene and Acetylene Adsorption on the Rhodium Catalyst.

Six experiments were conducted on the rhodium catalyst after a static exchange between tritium and hydrogen remaining on the surface after reduction. The results of the ethylene experiments are shown in table 24 and those of the acetylene experiments in table 25.

TABLE 24.

Ethylene Adsorption after Static Tritium Exchange

Catalyst, Rh/Al_2O_3 Temperature 200°C in experiments I & II

100°C in experiment III

Helium-treatment time, 5 hours in each experiment

Experiment & Injection Number.	Eluant Analysis						Hydrocarbon recovered as % carbon injected.
	Methane		Ethane		Ethylene		
	ml	cpm1.10^{-5}	ml	cpm1.10^{-5}	ml	cpm1.10^{-5}	
I.1.	0.03	0.4	0.18	0.4	-	-	37
2.	0.005	0.6	0.20	0.4	0.03	0.5	46
3.	-	-	0.16	0.5	0.17	0.3	66
II.1.	trace		0.19	0.25	-	-	38
2.	-	-	0.13	0.25	0.12	0.2	50
3.	-	-	0.04	0.2	0.36	0.1	80
III.1.	-	-	0.02	0.02	0.42	0.005	88
2.	-	-	0.02	0.04	0.44	0.007	92
3.	-	-	0.01	0.06	0.44	0.01	90

TABLE 25.

Acetylene Adsorption after Static Tritium Exchange

Catalyst Rh/Al_2O_3 Temperature 200°C in experiment IV
100°C in experiment V
20°C in experiment VI

Helium-treatment time, 5 hours in each experiment.

Experiment & Injection Number.	Eluant Analysis				Hydrocarbon recovered as % carbon injected.
	Ethylene	$ml\ cpm1.10^{-5}$	Acetylene	$ml\ cpm1.10^{-5}$	
IV.1.(200°C)	0.1	0.4	0.07	-	16
2.	0.02	0.3	0.25	-	54
3.	0.02	0.3	0.29	-	61
V.1.(100°C)	-	-	0.41	-	82
2.	-	-	0.43	-	86
VI.1.(20°C)	-	-	0.46	-	92
2.	-	-	0.49	-	98

Trace yields (< .005ml) of ethane and methane were recovered from injection IV.1.

4.3.iv Ethylene and Acetylene Adsorption on the Platinum Catalyst.

Two experiments were conducted on the platinum catalyst after a static exchange between tritium and hydrogen remaining on the surface after reduction. The results of the experiments are shown in tables 26 and 27.

TABLE 26.

Ethylene Adsorption after Static Tritium Exchange

Catalyst Pt/Al_2O_3 Temperature, 200°C

Experiment & Injection Number.	Eluant Analysis				Hydrocarbon recovered as % carbon injected.
	Ethane ml	Ethane cpml.10^{-5}	Ethylene ml	Ethylene cpml.10^{-5}	
I.1.	0.21	0.6	0.10	0.4	62
2.	0.07	0.4	0.40	0.25	94
3.	0.04	0.35	0.47	0.2	102

TABLE 27.

Acetylene Adsorption after Static Tritium Exchange

Catalyst, Pt/Al_2O_3 Temperature, 200°C

Helium-treatment time, 4 hours.

Experiment & Injection Number.	Eluant Analysis				Hydrocarbon recovered as % carbon injected.
	Ethylene		Acetylene		
	ml	cpml.10^{-5}	ml	cpml.10^{-5}	
II.1.	0.03	0.2	0.12	-	32
2.	0.03	0.1	0.30	-	66
3.	0.03	0.1	0.47	-	100

Ethane (0.01 ml 0.7 cpml.10^{-5}) was recovered from injection II.1.

4.3.v.Ethylene and Acetylene Adsorption on Alumina

Two experiments were conducted to investigate the adsorption of tritium, and subsequently injected hydrocarbon, by the catalyst support. Both experiments were made at 200°C and although the count rate was constant and equal to the background count rate after only 1½-2 hours, the helium flow was continued for five hours: this time was comparable with that in previous experiments. Recoveries of 95 and 98% for ethylene and acetylene respectively, were recorded and no activity was detected in either hydrocarbon.

4.3.vi Tritium and Subsequent Ethylene Adsorption on the Catalysts.

No attempt was made in the experiments described so far to calculate the amount of tritium retained by each catalyst. This was done in the following experiments.

An injection of 2ml of tritium (20 μc) was made into the helium stream above the catalyst as soon as possible after the helium flow was commenced after the reduction. The activity injected corresponded to 1.6×10^7 counts at the standard flow rate of $60 ml.min^{-1}$. The total count observed in the eluant before background was reached is shown in table 28.

TABLE 28.

Desorption of "Hydrogen" by Helium Treatment at 200°C.

Experiment Number and Catalyst.	Time of Helium Treatment before Injection (min)	Total Eluant Count ($x10^{-3}$)	Time to reach background.
I Palladium	11	235	11 hours
II Palladium	15	252	5½ hours
III Rhodium	10	70.5	4 min
IV Rhodium	23	62	6 min
V Platinum	3	175	31 min
VI Platinum	20	47	10 min

When, as indicated by the count rate, tritium had stopped desorbing from the catalyst, two or more 0.5 ml injections of ethylene were made over the catalyst. The full analyses of these injections are shown in table 29.

TABLE 29.

Full Analysis of Ethylene Adsorption on Tritiated Catalysts.

Experiment & Injection Number.		Eluant Analysis: Methane ml	Methane cpm1.10^{-5}	Ethane ml	Ethane cpm1.10^{-5}	Ethylene ml	Ethylene cpm1.10^{-5}	Hydrocarbon recovered as % carbon injected.
I Palladium	1.	0.01	18	0.30	12.5	-	-	61
(7 min)	2.	-	-	0.28	9.6	0.04	23	64
II Palladium	1.	0.01	10	0.27	12.9	-	-	55
(8 min)	2.	-	-	0.25	10.3	0.07	18.6	64
III Rhodium	1.	0.02	0.8	0.23	6.5	0.01	2	50
(75 min)	2.	-	-	0.18	5.7	0.01	2	38
IV Rhodium	1.	0.01	0.3	0.27	4.8	-	-	55
(8 min)	2.	-	-	0.16	3.1	0.10	1.6	52
V Platinum	1.	-	-	0.08	6.1	0.38	2.2	92
(16 min)	2.	-	-	0.03	2.8	0.48	1.4	102
VI Platinum	1.	-	-	0.07	7.1	0.30	2.3	74
(24 min)	2.	-	-	0.03	3.4	0.42	1.3	90

The figure in parenthesis is the time between successive injections.

4.3.vii.Summary

TABLE 30.

Percentage of Initial Hydrocarbon Dose retained by the Catalysts.

(a) in static exchange experiments.

	Ethylene		Acetylene		
	100°C	200°C	20°C	100°C	200°C
Palladium	-	45,47,41	-	78	86
Rhodium	12	63,62	8	18	84
Platinum	-	38	-	-	68

(b) in flow exchange experiments.

Palladium	-	39,45	-	-	-
Rhodium	-	50,45	-	-	-
Platinum	-	8,26	-	-	-

TABLE 31.

Specific Activity of Ethane recovered from First Injections of Ethylene at 200°C

	Specific Activity ($cpml.x10^{-5}$)	
	(a) in static exchange experiments.	(b) in flow exchange experiments.
Palladium	1.7, 2.1, 0.9	12.5, 12.9
Rhodium	0.4, 0.25	6.5, 4.8
Platinum	0.6	6.1, 7.1

TABLE 32.

Comparison of the Specific Activities of Ethane and Ethylene.

(Results are only recorded when both components were obtained in yields of greater than 10%. This was never the case in any acetylene experiment and seldom in the first injection of an ethylene experiment).

Specific Activities (cpml.x10^{-5})

	(a) in static exchange experiments.		(b) in flow exchange experiments.	
	Ethane	Ethylene	Ethane	Ethylene
Palladium	1.4	0.5	never sufficient ethylene	
	1.6	0.9		
	1.4	0.8		
	0.6	0.2		
	0.4	0.2		
Rhodium	0.5	0.3	3.1	1.6
	0.3	0.2		
Platinum	0.6	0.4	6.1	2.2
	0.4	0.25	7.1	2.3

4.4 Studies Involving C-14 Ethylene Adsorption on the Catalysts.

4.4.i Presentation of Results.

The "C-14 ethylene experiments" were designed to investigate the properties of the unrecovered portion of the initial 0.5ml dose of hydrocarbon. The procedure, detailed in section 3.8.c. involved one or more injections of labelled ethylene after approximately five hours helium treatment at 200°C. In separate experiments, subsequent injections of inactive ethylene, acetylene and hydrogen tested the reactivity of the residue in exchange, displacement and hydrogenation reactions. The investigation covered Pd/Al_2O_3, Rh/Al_2O_3 and Pt/Al_2O_3 at 20, 100 and 200°C.

The results are presented as full analysis tables, with a separate section for each residue treatment on each catalyst, i.e. studying temperature variation within each set of results. Injections of labelled ethylene are indicated by an asterisk. The proportion of the initially adsorbed radioactivity recovered from the first injection of inactive material, when significant, is shown.

4.4.ii Ethylene Exchange on the Palladium Catalyst.

The catalyst pretreatment was the standard one for this section (4.4) in which the catalyst was

reduced at 200°C for one to two hours and "cleaned" by flowing helium at 200°C for five to six hours.

Experiment II was designed to discover whether species adsorbed from second and third injections were more reactive than those from the first.

TABLE 33.

Ethylene Exchange with Ethylene Residues on the Palladium Catalyst.

Experiment & Injection Number.	Eluant Analysis: Methane ml	Methane cpm1.10^{-5}	Ethane ml	Ethane cpm1.10^{-5}	Ethylene ml	Ethylene cpm1.10^{-5}	Hydrocarbon recovered as % carbon injected.
I.1*(200°C)	0.01	0.02	0.30	0.42	0.015	0.07	64
2.	0.005	-	0.25	-	0.11	-	72
II.1*(200°C)-	-	-	0.25	0.48	0.03	0.18	56
2*	-	-	0.15	0.42	0.16	0.38	62
3*	-	-	0.06	0.35	0.34	0.34	80
4.	-	-	0.04	-	0.39	-	86
III.1*(100°C)-	-	-	0.09	0.30	0.31	0.38	80
2*	-	-	0.03	0.15	0.42	0.40	90
3	-	-	0.01	0.01	0.45	-	92
IV.1*(20°C)	-	-	0.02	0.08	0.42	0.39	88
2*	-	-	-	-	0.49	0.40	98
3	-	-	-	-	0.50	0.005	100

4.4.iii Acetylene Displacement on the Palladium Catalyst.

The catalyst pretreatment was again standard and multiple radioactive injections were made in all except the first experiment to find out whether the catalyst would retain any ethylene which could be displaced by acetylene.

TABLE 34.

Acetylene Displacement of Ethylene Residues on the Palladium Catalyst.

Experiment & Injection Number.	Eluant Analysis: Methane ml	Methane cpml.10^{-5}	Ethane ml	Ethane cpml.10^{-5}	Ethylene ml	Ethylene cpml.10^{-5}	Hydrocarbon recovered as % carbon injected.
I.1*(200°C)	0.01	0.01	0.31	0.45	0.01	0.24	65
2.(C_2H_2)-	-	-	0.04	-	0.005	-	9
II.1*(200°C)	0.01	0.01	0.31	0.47	-	-	63
2*	-	-	0.29	0.45	0.06	0.4	70
3.(C_2H_2)-	-	-	0.04	-	0.01	-	10
III.1*(100°C)-	-	-	0.10	0.20	0.30	0.47	80
2*	-	-	0.02	0.08	0.43	0.43	90
3*	-	-	0.02	0.05	0.45	0.41	94
4.(C_2H_2)	-	-	-	-	0.02	-	4
IV.1*(20°C)	-	-	-	-	0.42	0.36	84
2*	-	-	-	-	0.48	0.32	96
3*	-	-	-	-	0.47	0.29	94
4.(C_2H_2)	-	-	-	-	0.02	0.01	10

4.4.iv Hydrogenation of Ethylene Residues on the Palladium Catalyst.

An attempt was made to put hydrogen treatment, a proven method for the reactivation of the catalyst, on a quantitative basis by making 0.5ml injections of hydrogen on to the catalyst.

TABLE 35.

Hydrogenation of Ethylene Residues on the Palladium Catalyst

Experiment & Injection Number.	Eluant Analysis						Hydrocarbon recovered as % carbon injected.
	Methane		Ethane		Ethylene		
	ml	cpml.10^{-5}	ml	cpml.10^{-5}	ml	cpml.10^{-5}	
I.1*(200°C)	0.01	0.005	0.20	0.42	0.08	0.15	57
2*	-	-	0.15	0.38	0.20	0.30	70
3.(H_2)	0.005	0.01	-	-	-	-	-
II.1*(100°C)	0.01	-	0.06	0.21	0.36	0.36	84
2*	-	-	0.03	0.13	0.47	0.40	100
3*	-	-	0.02	0.11	0.49	0.38	102
4.(2mlH_2)-	-	-	0.02	0.10	-	-	-
			Recovery,25%				
III.1*(20°C)	-	-	0.01	0.06	0.46	0.39	94
2*	-	-	-	-	0.50	0.40	100
3.(2mlH_2)-	-	-	0.03	0.10	-	-	-
			Recovery,100%				

4.4.v Ethylene Exchange on the Rhodium Catalyst.

Having established a general lack of reactivity for the residues on palladium, the investigation of rhodium and platinum was conducted less extensively. The results, shown in the following sub-sections, were obtained using standard pretreatment conditions of one hour in hydrogen and five hours in helium, both at 200°C.

TABLE 36.

Ethylene Exchange with Ethylene Residues on the Rhodium Catalyst.

Experiment & Injection Number.	Eluant Analysis: Methane ml	Methane cpml.10^{-5}	Ethane ml	Ethane cpml.10^{-5}	Ethylene ml	Ethylene cpml.10^{-5}	Hydrocarbon recovered as % carbon injected.
I.1*(200°C)	0.02	0.02	0.22	1.0	-	-	46
2	-	-	0.17	-	-	-	34
3	-	-	0.18	-	0.08	-	52
II.1*(20°C)-	-	-	-	-	0.49	0.41	98
2	-	-	-	-	0.48	-	96

4.4.vi Acetylene Displacement on the Rhodium Catalyst.

TABLE 37.

Acetylene Displacement of Ethylene Residues on the Rhodium Catalyst.

Experiment & Injection Number.	Eluant Analysis: Methane ml	Methane cpml.10^{-5}	Ethane ml	Ethane cpml.10^{-5}	Ethylene ml	Ethylene cpml.10^{-5}	Hydrocarbon recovered as % carbon injected.
I.1*(200°C)	0.005	0.2	0.27	0.87	-	-	54
2.(C_2H_2)-	-		0.01	-	-	-	2
II.1*(100°C)	0.01	-	0.07	0.38	0.23	0.41	61
2.(C_2H_2)-	-		-	-	0.015	-	29

Acetylene (0.13ml and inactive) was recovered only from injection II.2.

4.4.vii Hydrogenation of Ethylene Residues on the Rhodium Catalyst.

TABLE 38.

Hydrogenation of Ethylene Residues on the Rhodium Catalyst

Experiment & Injection Number.	Eluant Analysis: Methane ml	Methane cpml.10^{-5}	Ethane ml	Ethane cpml.10^{-5}	Ethylene ml	Ethylene cpml.10^{-5}	Hydrocarbon recovered as % carbon injected.
I.1*(100°C)-	-		0.11	1.0	0.25	0.8	72
2.(H_2)	0.02	1.1	-	-	-	-	-

Recovery 15%.

4.4.viii Ethylene Exchange on the Platinum Catalyst.

TABLE 39.

Ethylene Exchange with Ethylene Residues on the Platinum Catalyst.

Experiment & Injection Number.	Eluant Analysis				Hydrocarbon recovered as % carbon injected.
	Ethane		Ethylene		
	ml	cpml.10^{-5}	ml	cpml.10^{-5}	
I.1*($200^{\circ}C$)	0.22	0.42	0.04	0.10	52
2*	0.08	0.23	0.35	0.33	86
3*	0.04	0.17	0.42	0.32	92
4.	0.03	-	0.44	-	94
II.1*($100^{\circ}C$)	0.005	0.08	0.46	0.35	92
2*	-	-	0.48	0.32	96
3.	-	-	0.49	-	98
III.1*($25^{\circ}C$)	-	-	0.48	0.41	96
2*	-	-	0.49	0.40	98
3.	-	-	0.50	-	100

4.4.ix Acetylene Displacement on the Platinum Catalyst.

TABLE 40.

Acetylene Displacement of Ethylene Residues on the Platinum Catalyst.

Experiment & Injection Number.	Eluant Analysis: Ethane ml	Ethane cpm1.10^{-5}	Ethylene ml	Ethylene cpm1.10^{-5}	Acetylene ml	Acetylene cpm1.10^{-5}	Hydrocarbon recovered as % carbon injected.
I.1*(200°C)	0.13	0.17	0.10	0.51	-	-	46
2*	0.04	0.10	0.31	0.25	-	-	70
3*	0.03	0.03	0.39	0.21	-	-	84
4.(C_2H_2)	-	-	0.04	-	0.23	-	54
II.1*(20°C)	-	-	0.46	0.24	-	-	92
2*	-	-	0.47	0.26	-	-	94
3.(C_2H_2)	-	-	0.005	-	0.41	-	86

4.4.x Hydrogenation of Ethylene Residues on the Platinum Catalyst.

TABLE 41.

Experiment & Injection Number.	Eluant Analysis				Hydrocarbon recovered as % carbon injected.
	Ethane		Ethylene		
	ml	cpml.10^{-5}	ml	cpml.10^{-5}	
I.1*(100°C)	0.01	.01	0.47	0.44	96
2*	-	-	0.50	0.38	100
3.(H_2)	0.01	.01	-	-	

Recovery, 50%.

4.4.xi. Summary.

TABLE 42.

Percentage of Initial Ethylene Dose retained by the Catalysts.

	Temperature (°C)		
	20	100	200
Palladium	12,16, 8.	20,20,16	43,36,44,35,37.
Rhodium	2	39,28	54, 46
Platinum	4, 8.	4, 8.	48, 54.

No exchange or displacement of residues occurred when inactive ethylene or acetylene was injected over a catalyst which had been previously dosed with C-14 ethylene (one to three injections). In the acetylene displacement experiments, however, although no significant recovery of activity was made, adsorption of acetylene occurred, as shown in table 43.

TABLE 43.

Percentage of First Subsequent Acetylene Dose retained by Catalysts.

	Temperature (°C)		
	20	100	200
Palladium	90	96	91, 90.
Rhodium	-	71	98
Platinum	4	-	46

These figures are not truly comparable due to the differing degrees of pre-saturation with C-14 ethylene: for the palladium catalyst, however, the magnitude and variation with temperature bear comparison with the initial retention results for acetylene shown in table 21. Hydrogenation experiments showed that when initial adsorption was small and complete saturation of the catalyst with C-14 ethylene was achieved, hydrogen could remove the adsorbed species. Removal was as methane from palladium at 200°C, rhodium at 100°C and platinum at 100°C and as ethane from palladium at 100 and 20°C. The quantities involved make quantitative estimations difficult.

CHAPTER FIVE

A DISCUSSION OF THE RESULTS

5.1. Introduction.

The results of the experiments detailed in chapter four are correlated and discussed with reference to the previous literature. Results from section 4.2. (Hydrocarbon Retention by the Palladium Catalyst), 4.3. (Hydrogen Retention by the Catalysts) and 4.4. (C-14 Ethylene Adsorption on the Catalysts) are discussed in the corresponding sections of this chapter (5.2., 5.3. and 5.4.) and an integrated discussion with particular reference to the retention of ethylene follows in 5.5.

5.2. Hydrocarbon Retention by the Palladium Catalyst.

5.2.i. Introduction.

In the experiments of section 4.2. the amount of retention of several hydrocarbons, by the palladium catalyst, was measured at three different temperatures, 20, 100 and 200°C. The observed variation is discussed in relation to,

(a) the degree of unsaturation in the hydrocarbon,

(b) the carbon chain length of the hydrocarbon,

and (c) the temperature of the catalyst.

The eluant analyses, which showed large yields of alkanes from the injection of alkenes, are discussed briefly.

5.2.ii. The Significance and Precision of the Results.

By comparison with the work of Cormack, Thomson and Webb,[75] and by considering the helium treatment as equivalent to evacuation, the measured adsorption is concluded to be that of the retained unreactive species observed by these workers. This is borne out by subsequent experiments (4.4.). The percentages, quoted in the summary tables in chapter four and reproduced below, do not correspond to fractions of measured monolayers as did those of Cormack et al.,[75] although approximate conversion to this figure is possible if certain assumptions, discussed below, are made.

Considering palladium in dispersed catalysts to expose mainly low index faces (100), (110) and (111), calculation shows that 1.2×10^{19} Pd atoms/m^2 of palladium surface area are exposed.[82] Calculation of the amount of gas required to give monolayer coverage, assuming different modes of adsorption[83] gives the following results,

No. of sites of attachment	1	2 contiguous	4 contiguous
ml of gas adsorbed/m^2 Pd	0.45	0.205	0.175

The metal surface area of the palladium catalyst used in

this study was determined, by Johnson, Matthey & Co. Ltd., by adsorption of carbon monoxide. Assuming that the carbon monoxide is adsorbed completely in the bridged form, a maximum metal surface area can be calculated to be $5.0 m.^2 g^{-1}$ of catalyst; conversely if the carbon monoxide is adsorbed totally in the linear mode the minimum metal surface area can be calculated to be $2.3 m.^2 g^{-1}$ of catalyst. From evidence of the proportion of each form found at saturation,[84] an intermediate value of $4 m.^2 g^{-1}$ is used in the calculation of the volume of gas corresponding to monolayer coverage of 0.5g of catalyst, the amount used in these studies.

No. of sites of attachment	1	2 contiguous	4 contiguous
ml of gas/0.5g of catalyst	0.9	0.4	0.35

Thus the injection size (0.5ml), chosen because it gave a conveniently measurable retention for ethylene, corresponds approximately to a monolayer coverage for two and four site attachment. Consequently, the retention measurements will not provide a means of distinguishing between these modes with any exactitude.

A second consideration concerning the quoted percentages is that, although they correspond approxi-

-mately to monolayer coverage, they were obtained from one injection only. Hydrocarbon was invariably recovered from the first injection, but only in a very few experiments was adsorption seen to be complete at this stage, i.e. retention of fractions of subsequent injections was usually observed.

The combined systematic and random error in the retention data is high, an indicated by the degree of reproducibility in the results from identical experiments (Tables 8, 12, 14 etc.). The percentage hydrocarbon retained by the catalyst is computed from a difference of two measured quantities, the peak areas of the calibration and reaction injections. The error in the retention value is therefore greatest when the retention is small. A precision of ± 3% in the estimation of peak area will be reflected in an error of ± 4 in individual experiments when retention is in the range 0 to 10%. When retention was of this order, i.e. in the adsorption of methane, ethane and propane only one experiment was carried out, except for propane adsorption at 200°C where, as shown in 4.2.vi., three experiments were conducted giving retentions of 13.5, 10 and 8.5%. When retention was greater, i.e. in the adsorption of all other hydrcarbons studied, experiments were repeated up to nine

times and consequently the percentage retention is a mean value and the error in it is considerably less. Table 21 is rearranged and reproduced below with approximate errors in parenthesis.

TABLE 21

Percentage of Initial Hydrocarbon Dose retained by Palladium Catalyst.

	20°C	100°C	200°C
Methane	2 (± 4)	4 (± 4)	4 (± 4)
Ethane	12 (± 4)	6 (± 4)	6 (± 4)
Propane	0 (± 4)	0 (± 4)	10.5(± 1.5)
Ethylene	33 (± 1.5)	31 (± 1.5)	40 (± 1.0)
Propylene	26 (± 2)	30 (± 2.5)	37 (± 2)
Cyclopropane	15 (± 4)	23.5(± 4)	31.5(± 2)
Acetylene	84 (± 1.5)	89 (± 1)	82 (± 1)

5.2.iii. Variation in Retention with Degree of Unsaturation in Hydrocarbons.

Taking account of these errors the retention figures can be seen to fall into three distinct groups, alkanes (0-10%), alkenes (26-40%) and acetylene (80-90%), whilst cyclopropane is most closely associated with the alkenes.

In a flow system it is not certain that the hydro-

-carbon does comes into equilibrium with the surface (Appendix p.122). Thus the rate of adsorption of a particular hydrocarbon will determine the proportion of an injection which is adsorbed. The rate of a process is partly controlled by the activation energy of the rate determining step: the lower the activation energy the faster the process. A low activation energy is, in turn, frequently associated with a high strength or heat of adsorption. It has been generally demonstrated[85] that an order of strength of adsorption for hydrocarbons on metal films is alkyne > alkene > alkane. Thus the three distinct classes of retention observed are a function of the relative strengths of adsorption. A further discussion of the origins of this order of retentions follows in section 5.5.

5.2.iv. Variation in Retention with Temperature and Carbon Chain Length.

Within the three hydrocarbon types studied, a variation in retention with temperature and carbon chain length was observed.

Detailed consideration of the individual alkane retentions as a function of temperature is prohibited by the large errors involved. At 200°C, however, there is evidence of a trend in retention of propane > ethane > methane. The same order was obtained

from studies of the reactivity of these compounds in exchange reactions over metal films.[86] The trend in these reactions was ascribed to the relative strength of the C-H bond broken in adsorption i.e. the weaker the bond the easier is adsorption.

$$\text{e.g.} \quad C_2H_6(g) \rightarrow \underset{*}{C_2H_5} + \underset{*}{H}$$

That, in this present study the trend was only detectable at 200°C, where C-C bond fission was also evident is maybe due both to the low precision of these determinations and the possibility of residual hydrogen on the surface. The latter possibility was confirmed in the experiments of section 4.3.

The retentions of ethylene and propylene, though very similar to each other when considered along with those of the alkanes and acetylene, showed some characteristic differences. At each temperature studied, more ethylene than propylene was retained by the catalysts. Thus the effect of carbon chain length is the reverse of that observed with the alkanes. At 200°C both hydrocarbons showed a greater retention than at 20° or 100°C. At these temperatures there was no significant difference in retention for either hydrocaroon.

The temperature effect is probably due to an increase in the extent of dissociative adsorption. The

ease or extent of dissociative adsorption is known to depend markedly on the cleanliness of the surface.[52] In this present study, the temperature effect is not significant below 100°C and this is typical of supported catalysts. The study of ethylene retention as a function of temperature is common to all three types of investigation of the present study and is discussed in section 5.3. and 5.4.

In the retention of the alkenes, the correlation of the observed effect of carbon chain length with reactivity in deuterium exchange reactions is not as informative as in the alkane retention. This is due to the competitive hydrogenation reaction and the probability that exchange proceeds through an alkyl reversal mechanism[87] rather than a dissociative one. Thus when Bond et al.[88] conclude that "olefin exchange is easier for propylene" in a study of the exchange/hydrogenation of ethylene and propylene over a 5% Pd/Al_2O_3 catalyst they were measuring the relative extent of deuterium introduction into the alkene at approximately the same conversion to alkane, and finding more deuterated propylene than ethylene. This does not necessarily imply that propylene will dissociate more readily than ethylene but is rather interpreted as being a consequence of the lower

strength of adsorption of propylene. It must be remembered that these observations were made under conditions for total hydrogenation and the mutual irrelevance of such measurements and similar ones of adsorption and inter-hydrocarbon exchange on a clean surface has been frequently stressed.

Possibly a more informative experiment would be the comparative adsorption and self-hydrogenation of ethylene and propylene. This has been studied on films of platinum, palladium and nickel,[89] on all of which it was found that a larger proportion of propylene than ethylene was self-hydrogenated. This suggests that a larger proportion of the propylene adsorption is dissociative compared with ethylene, but in the absence of information about the volume of each gas required to form a monolayer absolute comparison of the amount of dissociative adsorption is not possible. It must therefore be postulated, to account for the results of the present study, that monolayer coverage of palladium requires less propylene than ethylene; this is probable, due to the steric effect of the methyl group.

An explanation for the greater adsorption of acetylene compared with ethylene has already been made in terms of the relative rate of adsorption and a full discussion will be given in section 5.5. when

evidence from the results of other experiments has been considered. Here it is sufficient to note that (1) the approximate factor of two in retention might be a reflection of the four-site adsorption which is required for ethylene to reach the "acetylenic residue" state, and which is frequently postulated for the unreactive form of adsorption;[70,75] and (2) the temperature effect is proportionately less and, unlike ethylene and propylene, shows no definite trend. This lack of temperature dependence of retention suggests that bond fission might not be as important in residue formation from acetylene as from the alkenes.

5.2.v. Total Retention Measurement.

In several experiments injection of hydrocarbon was continued until saturation of the surface with residues was complete or nearly so. The total volume of hydrocarbon retained by the catalyst before 100% recovery of the injected hydrocarbon was observed shows an even wider division of the alkane, alkene, acetylene retentions (Table 44). The table is presented as the total volume of hydrocarbon adsorbed by unit area of the palladium surface for uniformity with the data of sections 5.3. and 5.4. where this procedure is necessary to compare retention on different metals.

TABLE 44

Total Volume of Hydrocarbon Retained by the Palladium Catalyst.

	Volume Retained (ml)(m^{-2} of palladium)		
Temperature (°C)	20	100	200
Methane	0.02	0.02	0.02
Ethane	0.05	0.03	0.04
Propane	0.0	0.0	0.08
Ethylene	0.18	0.18	0.28
Propylene	0.1	0.1	0.3
Acetylene	> 0.5	> 0.5	> 0.5
Cyclopropane	-	0.1	0.18

Experiments were not conducted which would permit calculation of the total volume of acetylene adsorbed at any temperature or of cyclopropane at 20°C.

5.2.vi. Eluant Analysis.

The final and possibly most important observation from the first series of experiments concerns the eluant analyses, particularly from the injection of alkenes and acetylene. It was thought, when the study was commenced, that a flow of helium over the catalyst at the reduction temperature would remove most of the hydrogen and possibly all the reactive hydrogen ad-

-sorbed on the surface. This would have permitted calculation of the residue composition from reactant and product analyses as outlined in section 3.1. A small fraction of hydrogenated species was to be expected from alkene injection and calculation, assuming this to be totally from self-hydrogenation would give the composition of the residue.

The large yields of alkanes recovered, particularly at 200°C, implying surface residues at that temperature of C_2H_1 from ethylene, $C_2H_{1.2}$ from acetylene and C_3H_3 from propylene are considerably more hydrogen deficient than most reports[70,72] and cast doubt on the efficiency of the helium treatment for removing hydrogen from the surface. Allowing the helium to flow over the catalyst for longer periods had no significant effect (Table 8 and Section 4.2.vii). If the alternative assumption is now made, i.e. that the source of hydrogen in the alkanes is the residual hydrogen left on the catalyst surface after reduction, then it is found that the catalyst had supplied as much 1ml of hydrogen to the first four or five injections at 200°C of each of ethylene, acetylene and propylene. This exceeds by a factor of approximately two, the calculated monolayer coverage of palladium by hydrogen atoms.

Ethylene injections at 200°C always resulted in

the formation of some ethane. This suggests that both self-hydrogenation and residual hydrogen on the catalyst might be responsible for ethane production. The ability of palladium to accommodate hydrogen atoms interstitially makes it likely that the latter source was the major one. The efficiency of helium in the removal of surface hydrogen following reduction of the catalysts is discussed in the next section (5.3.). This study was extended to rhodium and platinum catalysts.

APPENDIX TO SECTION 5.2.

Equilibrium Considerations and the Butene Experiments.

The butene experiments cannot, for the reasons given in 4.2.viii., be considered within the main discussion on retention. The results obtained have, however, some relevance to the premise made in 5.2.ii. that the injected hydrocarbons are unlikely to have come into equilibrium with the catalyst.

The distribution of the butenes recovered from the first injection of each experiment (full analyses, Table 20) is given below together with equilibrium percentages at each temperature.

TABLE 45

Butene Distribution from But-1-ene Injections on Pd/Al_2O_3.

Reaction Temp (°C)	Experiment Number	Butene Analysis as % Total Butene		
		But-1-ene	t-But-2-ene	c-But-2-ene
220	I	12	55	33
"	II	12	56	32
"	Equilibrium	15	55	30
150	III	21	48	31
"	IV	19	49	32
"	Equilibrium	9.5	62	28.5
100	V	37	36.5	26.5
"	Equilibrium	6.7	66.3	27
20	VI	38	23	39
	Equilibrium	3	75	22

From these figures it is apparent that only at 220°C was equilibrium established.

It would be impossible to determine with any accuracy the relative rates of but-1-ene isomerisation and the reactions leading to hydrocarbon retentions. Assuming however that they are of the same order of magnitude and have activation energies of 10 kcal/mole, then rate theory indicates that the reaction rate will

be approximately halved for every 20 degree reduction in catalyst temperature. If as seems likely the activation energy of the rate-determining process leading to retention is higher, then the temperature effect will be proportionately greater and recalling that all retention values were recorded using a flow rate 1½ times that of the butene experiments "it is improbable that the hydrocarbon dose comes into equilibrium with the surface".

5.3. Hydrogen Retention by the Catalysts.

5.3.i. Introduction.

The experiments described in section 4.3. showed that, even after prolonged helium treatment, hydrogen, which was active in hydrogenation and exchange reactions, was present on all the catalysts. In the present section, in addition to further discussion of ethylene and acetylene retention by the catalysts, an attempt is made to evaluate the relative importance, over each catalyst, of this residual hydrogen and self hydrogenation in alkane production. Correlation is sought between this measure and other properties of the catalysts.

5.3.ii. The Effect of the Alumina Support.

The similarities in the behaviour of the three catalysts (Pd,Rh and Pt) compared with the expected

anomalous hydrogen capacity of palladium (5.2.vi.) demands that serious consideration be given to the role of the alumina support used in the present study. A preliminary experiment in the first series had confirmed that ethylene was not hydrogenated or retained by alumina, pretreated in the same way as the catalyst in the experiments of that section. Similar blank experiments were conducted in this series (4.3.v.). Count-rates due to the desorption of tritium fell to the background level much more quickly than in similar experiments with supported metals. Furthermore, the injection of ethylene and acetylene did not result in any significant retention, hydrogenation or exchange.

Hall et al.[90] have studied the role and nature of "Hydrogen Held by Solids" and found that hydrogen was retained by alumina as surface hydroxyl groups. Adsorption of this hydrogen could only be observed after the most stringent evacuation procedures and its exchange with deuterium only at elevated temperatures. In the most pertinent report, in which the hydrogen retained by a 0.75% platinum/alumina catalyst was investigated, it was concluded that although there was more hydrogen present on the alumina than on the platinum ($\sim$ 20:1) the reactivity

of the hydrogen on the metal was, as expected, much greater. This reactivity was studied using the deuterium exchange reaction in which the complete monolayer of hydrogen on platinum was observed to exchange to equilibrium below 0°C while the rate of exchange with the alumina-bonded hydrogen only became significant at approximately 150°C.

In a study by Gruber,[91] of the chemisorption of hydrogen on a 1% platinum/alumina catalyst the relative amounts adsorbed on the metal and support were of the order of 10:1. Adsorption on the support was slow, taking approximately 20 hours for equilibration at 250°C compared with 2 hours for the metal. This probably represents a truer estimation of the contribution of the support in the present study and it is considered, on the evidence of the above results, the control experiments of Cormack et al.[75] and those of the present study, that adsorption and reaction with hydrogen does not occur on the support. The possibility of support participation is not however totally discounted and will be discussed later (5.3.iv.).

5.3.iii. Variation in Ethylene Retention on the Catalysts.

Differences in the retention of ethylene by the three catalysts are observed, but as indicated in section 5.2.v., in order to make quantitative comparisons the data must be normalised so as to apply

to a specific surface area. From the total, and metal, surface areas shown in table 1, it can be seen that, even if the alumina participates in some way, differences in behaviour are unlikely to be a function of the alumina areas since these are similar for the three catalysts.

TABLE 1

Catalyst Surface Areas

	Total Surface Area (N_2) ($m^2 \cdot g^{-1}$)	Metal Surface Area (CO) ($m^2 \cdot g^{-1}$ of catalyst)
Palladium	111	5.0
Rhodium	141	0.8
Platinum	147	0.2

From comparison of tables 21 and 30, retention of ethylene by palladium from the initial injection of the hydrocarbon is observed to be approximately the same despite the fivefold increase in the helium-treatment time. Eluant analysis (e.g. table 7 and 22) indicates that, if anything, more hydrogenation occurred when the helium treatment was prolonged. From these observations it might be concluded that, except for a short initial period, the catalyst behaviour is independent of the

time of helium pretreatment and the system used in this and the following section 4.4 is "catalytically equivalent" to that used in 4.2. where the helium-pretreatment time was much shorter.

The form of summary table 30 is not useful for the comparison of hydrocarbon retention on the different catalysts, since the percentages quoted apply to different surface areas of the metal involved, and table 46 is presented for this purpose. The figure given is the total volume (ml) of hydrocarbon adsorbed (5.2.v.), per unit area (m^2) of the catalyst metal. The palladium surface area used in these calculations was $4.0 m^2.g^{-1}$ of catalyst (5.2.ii.).

TABLE 46

Total Volume of Ethylene Retained by the Catalysts.

	Volume Retained ($ml.m^{-2}$ of metal)	
Temperature (^oC)	100	200
Palladium	-	0.6
Rhodium	0.4	3
Platinum	-	2

With the reservations made in section 5.2.ii. regarding the accuracy of single experiments (retentions

on platinum and rhodium at 100° were only determined once) for ethylene retention at 200°C, the following trend is observed;

$$Rh > Pt > Pd$$

This sequence is the same as that observed when metal films are used to study (a) the heat of adsorption of ethylene[92]; (b) reactivity for hydrocarbon cracking[58]; and (c) ability to catalyse alkane-deuterium exchange.[86] These correlations provide further evidence for the postulate that the inactive, retained species is formed by dissociative adsorption. Unlike the results obtained previously[75], the position of palladium in this sequence is not anomalous. However, it should be noted that;

(a) the present comparison is made from results at 200°C, rather than 20°C as previously,

and (b) whereas the rhodium and platinum catalysts were from the same stocks as used previously, the palladium catalyst was from a different batch.

Whilst the time of the helium pretreatment did not affect either the <u>initial</u> retention values or eluant analyses using the palladium catalyst, the <u>total</u> retention of ethylene on palladium at 200°C

after helium pretreatment for five hours was approximately twice that observed after a helium pretreatment for one hour (Tables 44 and 46).

A possible explanation is that there are two forms in which ethylene can be adsorbed on the catalyst, neither of which is removed by flowing helium: therefore both forms contribute to retention. One type may be more strongly bonded to the catalyst than the other and adsorption of the strongly bonded form evidently occurs from the initial injections, regardless of the hydrogen coverage of the catalyst. It is possible that the more weakly bonded form cannot displace hydrogen and this form of adsorption may only arise as hydrocarbon retention approaches saturation. Thus <u>initial</u> retention, which is predominately of the first type, shows no difference when the helium pretreatment is extended. <u>Total</u> retention is however dependent on both types and the increase in the more weakly bound component can be ascribed to a longer time in flowing helium (Table 46) and this is reflected in the increased total adsorption.

Support for this postulate as applied to all three catalysts is found in the reaction of the residue with hydrogen (4.4.xi.). Hydrogenated species are only recovered upon hydrogen injection, after presaturation of the catalyst with ethylene, and not if ethylene

injections are stopped while a large proportion of each is still being lost to the catalyst i.e. only the more weakly retained species can be "hydrogenated off" the catalyst.

Further discussion of ethylene retention as observed in the experiments of section 4.4. follows in section 5.4.

5.3.iv. Chemical and Radiochemical Eluant Analysis from Ethylene Injection.

The principal aim of the investigations of the hydrogen retained by the catalyst was to assess the relative importance of self-hydrogenation and hydrogenation by residual hydrogen in the production of the saturated species from the injection of alkenes. To do this absolutely the hydrogen used in reduction and the hydrogen in the reactants should be of different isotopes and 100% isotopically pure. Tritium was considered potentially more useful than deuterium because of the easier incorporation into a flow system of a very sensitive detector which would continue to permit a fast analysis and in addition provide a continuous monitoring facility of the eluant. Thus the efficiency of helium for hydrogen removal over each catalyst could be assessed in two ways; (1) by measuring the amount of hydrogen removed by the helium,

and (2) by measuring the incorporation of tritium in the eluant from hydrocarbon injections. Tritium was not available under pressure for flow reduction of the catalysts and two exchange procedures were adopted (3.8.b and d.). Only in the latter experiments (procedure d) was the total amount of tritium, removed by helium, measured.

Owing to an uncertainty in the background count-rate (3.8.d.) the cessation of tritium desorption could not readily be established. After four or five hours, however, the count-rate was observed to be constant and very close to the predetermined background level and injections of hydrocarbon were made. The high specific activity in the eluant from these indicated that on the surface of each catalyst there was a large amount of "residual" hydrogen which was reactive both in hydrogenation and exchange. Three quantities necessary for the consideration of the contribution of "residual hydrogen" are presented in Table 47. The volumes of gas quoted apply to 0.5g of each catalyst and the data of columns 1 and 2 were obtained at 200°C by continuing injections of ethylene until little or no ethane was recovered or ethylene retained by the catalysts.

TABLE 47

	Total Volume of Gas (ml) Ethane Eluted	Ethylene Retained	Hydrogen for Monolayer (ml)
Palladium	1.2	1.2	0.4
Rhodium	0.6	1.2	0.08
Platinum	0.3	0.2	0.02

Laying aside for the present the possibility of reactive hydrogen on the support and also ignoring the problem of the accommodation of the adsorbed ethylene residues, it can be seen from this table that residual hydrogen from the reduction, and self hydrogenation can account (within experimental error) for all the ethane recovered. Furthermore it can be appreciated that the latter is likely to be the more important mode of production especially over rhodium and platinum.

The specific activity of ethane eluted from the first injection over each catalyst was as follows:-

Pd, 1.6×10^5 cpml Rh, 0.4×10^5 cpml Pt, 0.6×10^5 cpml

The activity of hydrogen present on the surface was of the order of 2.0×10^5 cpml (figure 10). Whilst, therefore, these activities show the same order of dependence on self hydrogenation as above,

Rh > Pt > Pd

the magnitude of the dependence particularly for palladium would seem to be lower than the data of table 47 might suggest (Table 48).

TABLE 48

	Minimum Dependence on Self-Hydrogenation (as % from Table 47)	Dependence on Self-Hydrogenation (as% from activity measurements)
Palladium	66	20
Rhodium	87	80
Platinum	87	70

These latter figures are very dependent on the value given to the specific activity of the hydrogen on the catalyst surface. This cannot be estimated with any great precision due to the exchange method of tritiating the surface and the approximate agreement for rhodium and platinum is surprising and probably fortuitous. Since the heats of adsorption of hydrogen on all three metals are similar it is probable that the tritium exchange technique has been equally efficient on all three catalysts and that the relative result still stands, that self-hydrogenation of ethylene is much easier over rhodium and platinum than over palladium.

That there may take place some activation of

the hydrogen on the alumina as a result of the presence of the metals cannot be dismissed.[90] The greater dependence of palladium on residual hydrogen, however, would seem more easily explained in terms of interstitial accommodation in the metal rather than by an increased activation by palladium of the hydrogen on its alumina support: the alumina surface in this case was 25% less than for the others. The results of Hall and Lutinski,[90] although not obtained from the same type alumina as that used in the present study, suggested that, below 200°C, 1/5 of the 4.7ml $H_2/100m^2$ Al_2O_3 on a 1% platinum/alumina catalyst was exchangeable with deuterium. This would give a reactive hydrogen quantity on the catalysts of the present study of 0.5ml/0.5g of catalyst. The chemisorption results of Gruber,[91] on the other hand, indicate that only 0.03ml of desorbable hydrogen exists on the alumina of 0.5g of a similar alumina/platinum catalyst at 200°C. Thus although participation of the support, in accommodating some of the residual hydrogen, is possible, the actual amount and its reactivity cannot be clearly established. Furthermore, it does not explain the behaviour of the catalysts in terms of their relative abilities to retain hydrogen.

The accommodation of the large volumes of hydrocarbon adsorption will be discussed in section 5.4.

The comparative specific activities of ethane and ethylene (Table 32) from the first type of experiment using tritium (3.8.b) are in the ratio

for Pd, 2.5 , Rh, 1.5 and Pt, 1.5

This suggests either (a) palladium is less effective in alkene exchange than the other two metals (specific activity of ethylene low), or (b) palladium is less effective in self-hydrogenation (specific activity of ethane high). Bond et al.[88] established the order Rh > Pd > Pt for alkene exchange over 5% alumina supported metal catalysts. Hence it is concluded that the self-hydrogenation effect is the major one.

5.3.v. Flow Exchange Experiments.

The studies of ethylene retention using the flow exchange technique (3.8.d.) show at 200°C the same order of magnitude of initial hydrocarbon retention per unit area of metal surface i.e.

Rh > Pt > Pd

as do the studies after static exchange. They also exhibit the same twofold difference in the activity of the ethane recovered from the palladium catalyst relative to the others (12.7 cf 5.5 and 6.6). An order

of relative activities of ethane: ethylene and total retention data cannot be established since only two ethylene injections were made in these experiments. Consequently saturation of the surface was not achieved nor was sufficient ethylene recovered from the palladium experiments to calculate its specific activity with any accuracy.

The extra information which these experiments were able to provide was (1) the approximate amount of tritium adsorbed or exchanged on to each catalyst surface; and (2) an accurate measure of the time of helium treatment required before tritium desorption from each catalyst ceased. The latter measurement was possible due to improvements in the counter performance (3.8.d). This information is shown in table 28.

TABLE 28

Desorption of "Hydrogen" by Helium Treatment at 200°C

Experiment No. and Catalyst.	Time of the treatment before HT injection. (min)	HT count in eluant ($\times 10^{-3}$ c. m^{-2} of metal)	Time to reach background
Palladium I	11	118	11 hours
II	15	126	5½ hours
Rhodium I	10	176	4 min
II	23	155	6 min
Platinum I	3	1750	31 min
II	20	470	10 min

The effect of interstitial accommodation of hydrogen by palladium is apparent from the time required for the count-rate to reach background level. The reproducibility of the total eluant count from platinum is seen to be much poorer than those from rhodium and palladium. This is generally true for most of the measurements made on all the catalysts and may be due to the small metal area of platinum. In this example however it is worth considering the implication of the other two measurements shown in table 28. Injections of tritium at 3 and 20 min are made onto platinum catalyst surfaces of widely

differing degrees of hydrogen coverage as indicated by the time required for the count-rate to fall to the background level (i.e. 31 and 10 min). The former injection was made before much of the hydrogen from the reduction had been removed, the latter after practically all the removable hydrogen had been desorbed. No such difference exists for the palladium and rhodium since in each case the time of both injections was such as for injection to be onto catalysts of similar hydrogen coverage i.e. almost saturated in the case of palladium and "clean" in the case of rhodium.

The amount of tritium retained by the surface is therefore dependent on the metal, on its hydrogen coverage at the time of injection and the energies of adsorption, exchange and migration of hydrogen. Owing to all these factors it would be unrealistic to compare the adsorption capacities of the catalysts quantitatively in terms of the metal alone.

5.3.vi. Variation in Acetylene Retention by the Catalysts.

TABLE 49

Total Volume of Acetylene Retained by the Catalysts.

	Volume Retained ($ml.m^{-2}$ of metal)		
Temperature (^{o}C)	20	100	200
Palladium	-	0.4	1
Rhodium	0.1	0.5	2.5
Platinum	-	-	5

Since surface saturation was never achieved with the palladium catalyst at 200°C, the only temperature at which all three catalysts were used, comparisons of the metals for the retention of acetylene cannot be made. It is worth noting, however, that the difference between the retention of ethylene and acetylene from the initial dose of each is not so great for rhodium as for palladium (Table 30) and that there is no difference at all when total retention is considered (table 46 and 49).

Rhodium is the only catalyst for which total retention data as a function of temperature can be discussed. The gross temperature effect, evident in

table 49, and the suggestion of a similar type of behaviour with palladium, when it was subject to longer helium pretreatments, indicates that, as expected, "cleanliness" of the catalyst surface is of more importance at lower temperatures. This is more clearly demonstrated in section 4.4. when the temperature dependence of ethylene retention was studied in detail using each catalyst.

5.3.vii. Chemical and Radiochemical Eluant Analysis from Acetylene Injection.

Only from the second and third injections of acetylene onto the palladium catalyst at 200°C was any acetylene-tritium exchange observed. The yields of acetylene (0.005 and 0.01ml) were very low to indicate anything other than the fact that exchange does indeed take place.

Comparative specific activities, of any of the eluted products, as a function of catalyst metal or temperature cannot be undertaken for the reasons shown in table 50.

TABLE 50

Specific Activities of Ethane and Ethylene from Acetylene Injection.

Hydrocarbon	Ethane	Ethylene	Ethylene
Temperature (^{o}C)	200	200	100
Palladium	1.7	non resolvable	0.9
Rhodium	none recovered	0.4	none recovered
Platinum	0.7	0.2	no experiment

From the results in columns 2 and 3, it might be suggested that a similar comparative lack of dependence on self hydrogenation exists for the production of ethylene from acetylene over palladium as was found over that metal for the production of ethane from ethylene (5.3.iv.).

5.4.C-14 Ethylene Adsorption on the Catalysts.

5.4.i. Introduction.

The aim of the experiments discussed in this section was to establish the reactivity of the fraction of ethylene retained by the catalysts. It was confirmed, that under most conditions this fraction was in fact the unreactive one observed in the work of Cormack et al.[75] It was also established, contrary to the finding of

that report, that acetylene did not remove the ethylene residue, although it was adsorbed, even after saturation of the catalyst with ethylene. These observations are discussed together with a further examination of the dependence of ethylene retention on the metal of the catalyst and the experimental temperature.

5.4.ii. Variation in the Retention of Ethylene by the Catalysts.

TABLE 51

Total Volume of Ethylene Retained by the Catalysts

	Volume Retained ($ml.m^{-2}$ of metal)		
Temperature (^{o}C)	20	100	200
Palladium	0.05	0.1	0.4
Rhodium	0.03	0.8	2.5
Platinum	0.3	0.6	5

These figures demonstrate the large dependence of total retention on temperature, expected on the basis of the concept of activated adsorption and the increased inhibitive effect, at lower temperatures, of the residual hydrogen coverage of the metal surface.

The temperature effect is so great for rhodium that the retention of ethylene by this catalyst is seen to have fallen below that by palladium at $20^{o}C$.

It must be borne in mind, however, that owing to their substantially smaller metal surface areas, the experimentally measured retention on rhodium and platinum is very small at 20°C. Consequently these retentions are subject to large errors. Thus all that can be said of retention as a function of the catalyst metal at 20°C is that it is not possible to determine an order of the relative quantities. Owing to the greater temperature dependence of retention by rhodium, however, it is possible that a different order might exist at 20°C than that determined at 200°C. It cannot be proven or discounted that this order might be the same as that established by Cormack et al.[75] i.e.

$$Pd > Rh > Pt$$

It is confirmed that the order established at 200° of

$$Rh \geq Pt > Pd$$

also exists at 100°.

5.4.iii. Reactivity of the Retained Ethylene.

Even after the near saturation of the catalyst surface with C-14 ethylene, no radioactive species were recovered from the subsequent injection of non-radioactive ethylene or acetylene on to any of the catalysts, at any temperature. The specific activity of the C-14 ethylene used in the pre-adsorption, and the background level of the counter were such that a

recovery of 1% of the retained species could have been established with certainty. Thus it must be concluded that, discounting the possibility of a very large isotope effect, the adsorbed residue will neither exchange with ethylene nor be displaced by acetylene.

Some recovery of residues was achieved by treatment with hydrogen. The extent of the recovery was dependent on experimental conditions (Table 52).

TABLE 52

Effectiveness of Hydrogen for the Removal of Retained Ethylene

Catalyst and Temperature (°C)	Hydrocarbon Recovered from first & last h.c. injection as % carbon injected.	Volume of Hydrogen Injected(ml)	Hydrocarbon Recovered by Hydrogen injection as % carbon retained.
Pd. 200	57, 70	0.5	2½ as CH_4
Pd. 100	84, 102	2.0	25 as C_2H_6
Pd. 20	92, 100	2.0	100 as C_2H_6
Rh. 100	72, 72	0.5	15 as CH_4
Pt. 100	96, 100	0.5	50 as C H_4

The optimum conditions for the recovery of residual species are seen to be a small initial adsorption and the continuance of injection until saturation. This result is

in good agreement with the postulate of 5.3. i.e. the completion of retention to saturation is by a weaker, more reactive mode of adsorption than that responsible for the high initial adsorption (> 0.1ml). It would appear also that the major product of the removal of the strongly bonded residue is methane. This is in general agreement with a large body of the literature on such residual species.[70] There are too many variables in the data of table 52 for the dependence of the product to be discussed in terms of the metal alone but the methane yields correlate with the known performance as cracking catalysts of rhodium and platinum as compared with palladium.[58]

5.4.iv. Acetylene Adsorption on Catalysts Pre-exposed to Ethylene.

Although no displacement of the ethylene residue was achieved by the injection of inactive acetylene, adsorption of the latter was observed to take place even after the catalyst had been almost saturated with C-14 ethylene. The extent of the adsorption was in most cases as great as that on the catalyst prior to the retention of any ethylene. The relevant data are presented in table 53.

TABLE 53

Percentage of the Initial Acetylene Dose Retained by the Catalysts.

Temperature (°C)	20	100	200
(a) on catalysts unexposed to ethylene (Tables 21 and 30)			
Palladium	84	84	84
Rhodium	8	18	84
Platinum			68
(b) on catalysts covered to various degrees with ethylene (Tables 34,37, and 40)			
Palladium	90 (6)	96 (6)	91 (32)
Rhodium		71 (39)	98 (46)
Platinum		14 (6)	46 (16)

The figure in parenthesis is the percentage of the ethylene injection, immediately before the acetylene one, which was retained by the catalyst.

When no displacement of the residue was observed from the first injection of acetylene the experiment was ended. Thus comparison of the total amount of acetylene adsorption which takes place after pre-saturation with ethylene cannot be discussed. From these initial retention results, however, and those

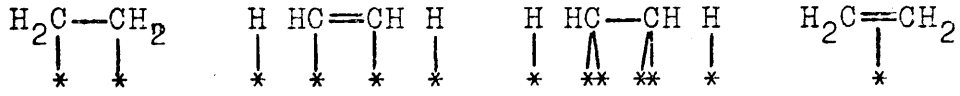
of the comparative total retention measurements (5.3.iii. & vi.) it must be concluded that more sites are immediately available for the adsorption of acetylene than for ethylene. The accommodation of this acetylene and the residual ethylene in excess of monolayer coverage (5.3.iv.) is discussed in the final section together with the possible modes of such adsorption.

5.5. Conclusions.

5.5.i. The Mode and Sites of Ethylene Retention.

Part of the adsorption of ethylene by catalysts in a helium flow system has proven to be the adsorption of a species inactive in hydrogenation and molecular exchange. Identification of the structure of this species has been one of the primary aims of this work (Chapter 2).

The principal modes of adsorption postulated for ethylene are as shown

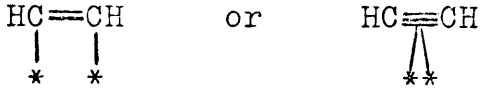


(a) (b) (c) (d)

In the present study, the magnitude and variation of retention on different catalysts and at different temperatures suggests that for all the catalysts studied the mode of adsorption leading to the inactive residue is dissociative i.e. (b) or (c). This is in agreement with the conclusions of Beeck[70] and of Jenkins and Rideal.[72]

The complete lack of reactivity of the ethylene residue with acetylene and the considerable adsorption of acetylene on catalysts presaturated with adsorbed ethylene suggests that the residue is,

(1) not present as a reactive form of chemisorbed acetylene which is considered to be an associatively bonded species i.e. either

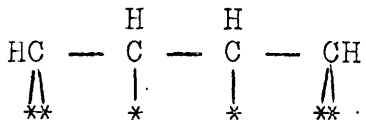


or (2) is not present on the same surface sites as the chemisorbed acetylene, i.e. the same surface exhibits different types of heterogeneity for different hydrocarbons.

Evidence has been postulated in previous studies of residues for both of these possibilities.

Chemical analysis of the products obtained on the removal of ethylene residues by hydrogen treatment at elevated temperatures most frequently resulted in the recovery of methane. More controlled treatment, however, of residues on nickel,[70] platinum[32] and palladium[64] has indicated that polymeric structures existed on the surface. Infra-red analysis of ethylene chemisorption, in addition to detecting the presence of various C_2 species has shown that on nickel,[30,33] platinum[32] and palladium,[30] supported on silica, there existed polymers mainly as

C_4 residues. These might be considered to be



though not necessarily linear as shown.

It has been calculated on the basis of a geometric effect[93] that adsorption of acetylene should take place on the longer (i.e. $\sqrt{2}$ a) and ethylene on the shorter (i.e. a) interatomic spacings of the face-centre cubic metals of group VIII. The argument is, however, developed on the basis of reactive associatively bonded species. Thus the results are of doubtful relevance to the present study.

If, then, the residues are accommodated on the surface as polymers, the relative extent of polymerisation might control the amount of each hydrocarbon retained. The polymerisation of acetylene is likely to be more extensive since the surface concentration of C_2H_2 groups will be greater from acetylene chemisorption than from dissociative ethylene adsorption, (b) or (c), which require four or six sites respectively.

There is, as has been observed previously, a considerable excess of the retention of both acetylene and ethylene over the measured CO monolayer. This could be accounted for by:

(1) experimental errors.

(2) the availability of more metal surface for the adsorption of ethylene and acetylene than for carbon monoxide. This might be possible by the removal of strongly bonded hydrogen which was unaffected by the evacuation procedure prior to the determination of the carbon monoxide surface area.[82]

(3) adsorption by the support either by migration from the metal or owing to activation of the support by the presence of the metal.

By virtue of their low metal surface areas, errors in the estimation of the eluants from the platinum and rhodium catalysts are substantially greater than those of the results from palladium. Excesses over monolayer coverage can, however, be no less than five-fold. A second possible flaw in the experiments is that slow desorption of the retained species might take place. If these were C_4 polymers there would be a further long delay in elution from the silica gel column the performance of which was optimised for the detection of C_2 species. This would result in unsaturated C_4 compounds being undetected unless present in large quantities (> 0.5ml).

The second possibility i.e. that the metal surface area is specific for each adsorbate is unlikely to account for the total excess retention. It has been found,[84] however, that heating in hydrogen at 100°C can reduce the amount of CO adsorption on a 5% Pd/Al_2O_3 catalyst from 105 to 46 cm^3/g Pd.

Adsorption on the alumina support is undoubtedly possible at high temperatures (>150°C). Indeed alumina is frequently the "support" employed in bifunctional catalysis where skeletal isomerisation is considered to take place on the "support". Infrared investigations by Yates and Lucchesi, and chemical studies by Sinfelt et al. have established that:

(1) the adsorption of ethylene and acetylene took place on alumina, the latter adsorption occurring much faster,[31]

(2) the surface species reacted with hydrogen at 450°C to give C_1 to C_3 alkanes,[32]

(3) the sites for the adsorption of ethylene and acetylene were mutually independent,[31]

(4) hydrogenation of ethylene took place on the alumina in the temperature range 120° to 430°C,[94]

(5) there was evidence for migration, on a Pt/Al_2O_3 catalyst, of reactive species between centres on the metal and on the

support,[32]

and (6) that the greater hydrogenation activity of Pt/SiO_2 compared with Pt/Al_2O_3 was due to the greater amount of chemisorption of ethylene by the alumina.[32]

Despite the lack of quantitative data on the amounts of adsorption on the alumina support material it seems probable that it will contribute to the measurements made in the present study. It is however not possible to establish whether the adsorption takes place directly on to "metal activated" sites on the alumina or by migration from the metal to the alumina.

The excess retention of ethylene and acetylene over the calculated monolayer coverage is thus considered to be a function of two possible effects: adsorption by the support and increased adsorption by the metal. In the absence for the lack of quantitative data, the support participation would appear to fit better most of the observed facts.

Correlation of the present results with the published work on residues has been made throughout the discussion sections particularly with reference to variations in the extent of residue formation on different catalysts and at different temperatures. There is in the results of the present study an agree-

-ment with the general findings of these experiments i.e.

1) that residues occur most readily on the surfaces with the minimum preadsorbed hydrogen,
2) that residues are only totally removable by hydrogen treatment at high temperatures.

5.5.ii. General Conclusions.

The relevance of the present work to general kinetic investigations of catalysis can be stated in the following way. Kinetic measurements have been made in flow systems[95,94] in which the reactants are either dosed or continuously bled into the carrier gas stream. The results of the present work demonstrate the necessity for caution in examining these rates and those obtained in static systems with particular reference to the interpretation of initial rates on clean catalysts. Irreversible adsorption will take place and the surface area of the catalyst will initially diminish rapidly. In continuously bled or static system this may happen fairly quickly and meaningful results on the remaining surface will be obtained. In a dosed system, however, depending on the proportion of reactant to catalyst surface area, it may be only after several injections that the catalyst will become of constant surface area.

Mechanistic studies of reactions, dependent largely as they are on rate data, require the same cautious interpretation as discussed above. In addition, the discovery of considerable retention by catalysts of hydrogen from the reduction period suggests that, possibly even in conventional vacuum systems, mechanisms of hydrogen exchange in hydrocarbons over supported catalysts would be best studied under conditions where the catalyst has been exposed only to an isotopically pure sample of the hydrogen isotope to be used in the exchange. This exposure should include as complete an exchange of the hydrogen on the alumina support as possible, in so far as this is compatible with maintaining a sufficient metal surface area.

A final conclusion from the present study with regard to the interpretation of previous results is the tenuous nature of any argument in explaining the relative activity of supported catalysts in terms of the physical properties of the metal involved. Less fundamental correlations with, for example, other catalytic properties, would probably be easier and in the long term more informative than those with work function, interatomic distances etc.

The above conclusions are of a very general and somewhat negative nature. More specific and positive

deductions can be made with regard to the protection and regeneration of catalysts from residue contamination. Residues, once formed, cannot be removed without heating the catalyst in hydrogen. If this is undesirable, i.e. catalyst sintering cannot be permitted, then residues should be prevented from being formed by carrying out reactions with a hydrogen rich mixture. In the few experiments where the activity of the catalyst was tested after saturation with ethylene residues, it was found active in the hydrogenation of ethylene, introduced in a 1:1:: hydrocarbon:hydrogen mixture. This might indicate that the residual species are located mainly on sites not responsible for the activity of the catalysts. If this is generally true, then residual species, once formed, should not affect the measurements made during reaction at the surface. Whether or not this is true, the temperature of the catalyst has a smaller effect on retention than the classically predicted effect on reaction rate. Thus in the range studied, (20 to 200°C) temperature increase would be expected to produce a net increase in the activity of the catalyst.

Comparison of the effect of different catalyst metals was difficult, as stressed throughout, because of the low surface areas of the rhodium and platinum

catalysts. Given, however, similar preparations of similar surface areas it would appear that palladium would be the least susceptible to the deposition of residues. This is almost certainly due to the "self-protection" afforded it by hydrogen accommodated in the interstices of the palladium lattice.

5.5.iii. Future Work.

The flow reactor-chromatograph as designed fulfilled most expectations. A difficulty encountered with regard to the investigation of residues, was the inability of flowing helium to remove the hydrogen left after the reduction treatment; this made futile the calculation of residue compositions. Whether or not this hydrogen could be removed by evacuation might be tested by providing a facility for the evacuation of the catalyst vessel.

In order to investigate quantitatively the extent of self-hydrogenation, if the "reduction" hydrogen proved immovable, deuterium could be used for the reduction of the catalysts and the saturated hydrocarbons recovered, analysed by mass spectrometry.

Deuterium could be similarly used to investigate the nature of the residues. Treatment of the residues with flowing deuterium and subsequent mass spectrometric analysis would indicate the exact hydrogen content of the species on the surface. Difficulties, however,

can be foreseen in removing the residues at a convenient rate for collection, without C-C bond fission occurring on the surface.

The interesting results of acetylene adsorption on a residue saturated catalyst demand that further attention be directed to this aspect of the work, i.e. subsequent and competitive retentions of different hydrocarbon types.

Finally the effect of the alumina support might be more thoroughly investigated either by replacing the hydrogen on it in some way e.g. fluoridation[90] or if the exact nature of mixed supports can be established, by varying the amount of alumina in a mixed support catalyst.

In conclusion, then, the flow system used, has provided much information about supported catalysts close to their working state and by the incorporation of a few minor alterations could yield even more informative results. These, however, will be governed by many variables which may or may not be ultimately controlled by the specific metal used. Thus, although the information obtained will be useful in a general understanding of catalytic activity, a fundamental approach to an understanding of the gas-solid interaction must be made by the elimination of as many

variables as possible and therefore by the observation of the interaction on the surfaces of single metal crystals prepared in ultra-high vacuum conditions.

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